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NBS/EPA Energy Environment Project

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TO
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENERGY, MINERALS, AND INDUSTRY
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FOREWORD

The role of the National Bureau of Standards (NBS) in the
Interagency Energy/Environment R&D program, coordinated by the
Office of Research and Development, U. S. Environmental Pro-
tection Agency, is to provide those services necessary to assure
data quality in measurements being made by a wide variety of
Federal, state, local, and private industry participants in the
entire program. The work at NBS is under the direction of the
Office of Environmental Measurements and is conducted in the
Center for Analytical Chemistry and the Center for Radiation
Research. NBS activities are in the Characterization, Measure-
ment, and Monitoring Program category and address data quality
assurance needs in the areas of air and water measurement
methods, standards, and instrumentation. NBS outputs in support
of this program consist of the development and description of
new or improved methods of measurement, studies of the feasi-
bility of production of Standard Reference Materials for the
calibration of both field and laboratory instruments, and the
development of data on the physical and chemical properties of
materials of environmental importance in energy production.
This report is one of a series issued every six months by NBS to
provide information to the Interagency Energy/Environment
community on the status of methods, standards and data projects
at NBS. Detailed project information is also provided in the
Interagency Energy/Environment Research and Development Series.

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INTRODUCTION AND SUMMARY

This report describes work performed by the National Bureau of Standards (NBS) during the period, July 1979 to December 1979, under the Interagency Agreement (EPA-IAG-D8-E684) between the U.S. Environmental Protection Agency and NBS. This Agreement covers the development of standards, methods, data, and instrumentation for quality assurance of measurements of pollutants associated with energy production and use. The highlights for this reporting period in the eight sub-agreement areas are given below.

80 BCKa - ENERGY RELATED POLLUTANT MEASUREMENT AND INSTRUMENTATION DEVELOPMENT

Under the task, "Energy Related Water Pollutant Analysis Instrumentation", a revised list of 23 marker compounds to be used in the Master Analytical Scheme were received. NBS has obtained, synthesized, and performed chemical and isotopic purity checks on most of the compounds. The chemical purity of the compounds was checked by gas chromatography or liquid chromatography and mass spectrometry. The isotopic purity of the compounds was also checked by mass spectrometry. All of the compounds tested thus far appear to be of satisfactory chemical and isotopic purity for their intended purpose, except for 1,2-dichloroethane-d_4.

Additional refinements have been incorporated into the liquid chromatography-mass spectrometry system (LC-MS): installation and calibration of a sensor, changes to optimize configuration location, and replacement of one of the vacuum flanges with a viewport and telescope to permit viewing the operation of the LC-MS interface probe in situ. The system has been applied to analytical problems and encouraging results were obtained. Patent application for the interface has been filed by EPA.

Work related to the measurement of trace organometallics using liquid chromatography-electrochemical detection (LC-EC) has focused on the development of electrochemical detectors. A new detector has been developed that enables measurements to be performed in a normal laboratory environment without sacrificing detection limits. In addition, an Interagency Energy/Environment Research and Development Program Report describing activities with the LC-EC technique was issued this reporting period (EPA-600/7-79-211).

Preliminary experiments with metal specific detectors and high performance liquid chromatography (HPLC) has shown some promise as an analytical technique for speciation of inorganic pollutants. Work is continuing on the development of methods using such an approach to identify and measure inorganic species in effluents.

80 BCKb - ENERGY RELATED WATER POLLUTANT ANALYSIS INSTRUMENTATION

Under the task, "Development of Measurement Methods for Non-Volatile Pollutants in Water due to Energy Technologies, experiments have been performed using the Raman microprobe technique to optimize the isolation of trace fractions in effluents, and to identify and measure components of the effluent.

Most of the reagents for labeling antibodies required for work on the development of specific immunoassays for dinitrophenols in water have been obtained. Work plans are underway to incorporate iodine-125 into the technique to provide a more specific procedure of antibody labeling.

80 BCLa - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
          ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

Under the task, "Development of SRM's for Stationary Sources Associated with Energy Production", mixtures of NO_2 in air at 250, 500, 1000, and 2500 ppm were evaluated for homogeneity; cylinders

of 50 and 90 ppm SO_2 in N_2 have been ordered, and prepared laboratory standards of these are under evaluation; and two new SRM's of 2 and 10 mole-% O_2 in N_2 have been certified. Under "Development of SRM's for Monitoring Ambient Air Impacted by Emissions Resulting from Energy Production", gravimetric standards of CO_2 in air at atmospheric concentration had a total estimated uncertainty not exceeding ± 0.1 percent relative; two additional Computer-Operated Gas Analysis Systems (COGAS-II and COGAS-III) were constructed, one to assist gas SRM certification, the second for automation of gas permeation tube calibrations; and a procedure for establishing traceability of commercial gas standards to NBS gas SRM's was reviewed by EPA (EMSL/RTP) and representatives of the Compressed Gas Association.

In the development and evaluation of standards for calibration of x-ray fluorescence particulate analysis, thin films were prepared from glass targets having low Z elements (S,P), and additional glass targets containing 5-6 elements of interest to EPA (having various elemental compositions) are under evaluation.

Under "Particulate Physical and Chemical Characterization", work on Particle Doppler Shift Spectrometry (PDSS) is heading into the submicrometer aerosol particle range, a developed theoretical model was found to agree well with experimental results, and PDSS was used to characterize several aerosol generators. Also, it was found that aerosol size of solid spherical particles generated from ammonium fluorescein solution by a vibrating orifice generator can be predictable.

Under "Particulates on Glass Fiber Filters", final certification of SRM 2673 (Sulfate and Nitrate on Filter Media) and SRM 2674 (Lead on Filter Media) was completed.

The bulk urban air particulate collection for Washington, DC, was completed, and the material was sieved and subjected to preliminary analyses for inorganic and organic constituents.

80 BCLb - ENERGY RELATED AIR POLLUTANT ANALYSIS INSTRUMENTATION

Under "Development of an Instrument to Measure Airborne Sulfate Particulate Matter", detector response was shown to be consistent with theory, and sensitivity was enhanced using a sulfur compound to dope the detector hydrogen gas. Further, it was shown that an alternate detector design could improve response time by a factor of 15, allowing for essentially full recovery of the potentially available response.

80 BCLc - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

Under "Radiocarbon as an Environmental Trace", using the NBS system for analysis of environmental samples containing only 5-10 mg carbon in several collaborative studies with industry and universities, it was generally observed that (1) urban particulates predominantly contain fossil carbon, and (2) particulates from remote locations contain less organic carbon (which is primarily biogenic). An exception to this was found in a study of air particulates in Portland, Oregon that were found to contain up to 100 percent biogenic (natural) carbon, illustrating an air pollution potential due to residential wood burning. In addition, collaborative work is underway for calibration of the new NBS International Radiocarbon Dating Standard for high accuracy radio-carbon measurements. Other advances have included the initiation of analysis of atmospheric methane, and the use of a tandem Van de Graaff accelerator to demonstrate a significant lowering of sample size requirements for measuring natural radiocarbon to 10 micrograms of carbon.

Under "Organics on Air Particulates", methodology has been developed and refined for quantitative characterization of polycyclic aromatic hydrocarbons (PAH) extractable from the NBS Urban Air Particulate SRM (SRM 1648). Various extraction procedures have been evaluated. Analytical methodology is based on normal phase HPLC fractionation, followed by analysis of the isolated PAH fractions by capillary column GC/MS, and by reversed-phase HPLC with fluorescence detection. Over 50 PAH derivatives have been identified.

80 BCMa - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

The task, "Energy Related Water Pollutant Standard Reference Materials", was initiated to develop energy related water pollutant Standard Reference Materials (SRM's) for conventional fossil fuel mining and combustion fuel technologies, with the Western areas of the U.S. being the primary focus of studies/activities. Work this reporting period focused on the completion and certification of Standard Reference Materials for Estuarine Sediment (SRM 1646), a re-issue of Trace Elements in Water (SRM 1643a), and Polynuclear Aromatic Hydrocarbons (SRM 1644) is in process.

Preliminary experiments with Matrix Isolation Laser Raman Spectroscopy have shown this technique to be technically and scientifically feasible for sequentially acquiring and analyzing data for complex mixtures of volatile organics. Efforts are underway to refine this technique so that it could be applied to the certification programs for SRM's for Trace Organics in Water.

80 BCMb - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

Activities under this task focused on the development of SRM's for organic water pollutants associated with emerging energy technologies. Significant progress was made on the analysis of

phenolic species in shale oil using several analytical techniques. More developmental work (e.g. stability studies, method refinement) leading to the production of a phenol in water SRM has been performed during this reporting period.

NBS participated in a round robin exercise to determine inter-laboratory precision on the measurement of phenols in waste waters. The phenol concentrations and pHs found for eight samples are reported.

80 BCN - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVLEOPMENT

Activities under the task, "Radiological Pollutant Quality Assurance", resulted in the preparation and submission (to EPA/ Las Vegas) of two hundred samples of fly ash assayed for radium-226 and radium-228. NBS also provided EPA/LV with seven solution reference samples as part of the measurement traceability program conducted with the EPA/LV laboratory.

1.   Energy-Related Water Pollutant Analysis Instrumentation

1.a.   Development of Marker Compounds

A revised list of 23 labelled compounds to be used in the Master
Analytical Scheme (and samples of two additional compounds) were
received in mid-December. One labelled (quinoline-d_7) and two
unlabelled compounds (bisphenol A and di-n-octyl ether) to be
provided by Research Triangle Institute/Gulf South Research
Institute (RTI/GSRI) have not yet been received.

Plans have been made for the preparation of the required 600
vials of six spiked solution mixtures, and for studies of the
stability of the six mixtures.

Synthesis of Labelled Compounds. Two labelled compounds were
to be synthesized by NBS. 2-Naphthalene sulfonic acid-d_7 has
been prepared with a mass purity of greater than 99 percent (as
determined by HPLC) and an isotopic purity of 98 percent (by
mass spectrometry). Unlabelled dodecylphosphoric acid has been
prepared from dodecanol as a model for the preparation of
dodecylphosphoric acid-d_{23} from dodecanol-d_{23}.

Chemical and Isotopic Purity of Marker Compounds. Table 1 lists
the current status of the chemical and isotopic purity checks.
Six compounds that were dropped in the latest list of marker
compounds, but for which data had been acquired, are not included.
Chemical purity has been checked by gas chromatography (GC) or
liquid chromatography (LC) for quantitative data and also by mass
spectrometry. Isotopic purity has been checked by mass spec-
trometry with results listed as satisfactory (S) since numerical
values have not yet been calculated from the mass spectra.

Table 1

Current Status of the Chemical and Isotopic Purity Checks

Compounds Available	Chemical Purity Quant. Method	% Impurities	Isotopic Purity
n-Butylamine-d_9			S
n-Butyric acid-d_7			
2-Naphthalenesulfonic acid-d_7	LC	<1%	S
Dodecylphosphoric acid-d_{23}			
Ethanol-d_6[a]			
Acetonitrile-d_3	GC	<1%	S
t-Butanol-d_{10}[a]	GC	ND	
1,2-Dichloroethane-d_4	GC	∿8%	S
Diethylether-d_{10}	GC	ND	S
Anisole-2,4,6-d_3	GC	<1%	S
Chlorobenzene-d_5	GC	ND	S
n-Decane-d_{22}	GC	ND	S
Naphthalene-d_8	GC	ND	S
o-Xylene-d_{10}	GC	ND	S
Nitrobenzene-d_5	GC	ND	S
Anthracene-d_{10}			S
Di-n-octylether-d_{34}	GC	ND	S
Quinoline-d_7			
Phenethylamine-d_4	GC	ND	S
Hexamethylenetetramine-d_{12}			S
Phenol-d_6[a]	GC	ND	S
Benzoic acid-d_5			S
Bisphenol A-d_{16}[a]			

ND = non-detected   S = satisfactory

[a] Isotopic purity checked/to be checked by H/D exchange with water giving purity for ethanol-d_5, t-butanol-d_9, phenol-d_5, and bisphenol A-d_{14}.

All of the compounds tested appear to be of satisfactory chemical and isotopic purity for the intended purpose, except for 1,2-dichloroethane-d_4. This compound appears to be contaminated with about 7 percent of 1,1,2-trichloroethane and 1 percent of 1,1,1,2-tetrachloroethane, as determined by electron capture GC. The presence of 1,1,2-trichloroethane-d_3 was confirmed by mass spectrometry.

1.b. Application of Selective Detectors to Liquid Chromatography

See Section BCK-a 1.e.

1.c. Liquid Chromatography-Mass Spectrometry

Changes made in the instrument since the last report include: installation and calibration of a sensor (to better determine the ion source temperature), changes in the heat sink at the probe tip (to find the optimum configuration), and replacement of one of the vacuum flanges with a viewport and telescope (to permit viewing the operation of the LC-MS interface probe _in situ_).

A determination of the maximum flow rates that the concentrator could accommodate was made and the results are shown in Table 2. LC/MS of heterocyclic compounds containing nitrogen gave the expected chemical ionization spectra at high source pressures, and spectra with more electron impact EI character at lower source pressures.

Table 2.   Concentrator Flow Rates

Solvent	ΔHv[a]	Maximum Flow Rate
n-pentane	90 cal/g	3.0 mL/min
i-octane	90 cal/g	2.8 mL/min
Methanol	260 cal/g	1.7 mL/min
50% Methanol/H_2O	410 cal/g	0.7 mL/min

[a]Heat of vaporization.

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Preliminary tests have been made with encouraging results for the direct determination of phenol in shale oil. The selectivity of the mass spectrometer as an LC detector enables us to obtain a clean phenol peak by monitoring at m/z = 94. The first determinations yielded a value that is about 10-20 percent higher than was obtained by other methods, but the stability of the response of the instrument is excellent, promising usefulness as a quantitative detector. (For example, the standard deviation of replicate standards is about 5%.) Comparison of the ultraviolet (UV) 254 nm chromatogram and the m/z=94 LC/MS single ion record obtained under identical HPLC conditions is made in figure 1.

When running direct injections of shale oil, some problem was experienced with the deposition of material on the end of the probe. A new end fitting has been designed but not yet constructed, using a Teflon diaphragm on the end of the probe. The flow control needle will perforate the soft material and it is hoped that the resulting orifice will be smaller and smoother so that the momentum of the exiting liquid will be sufficient to tear the liquid drops away from the end of the probe.

A description of the LC-MS concentrator and probe was presented at the American Society for Mass Spectrometry meeting in Seattle; and a patent application for the interface has been filed by EPA.

1.d. Feasibility Study of Application of Particulate Analysis by Ion Microprobe

No report issued for this report period.
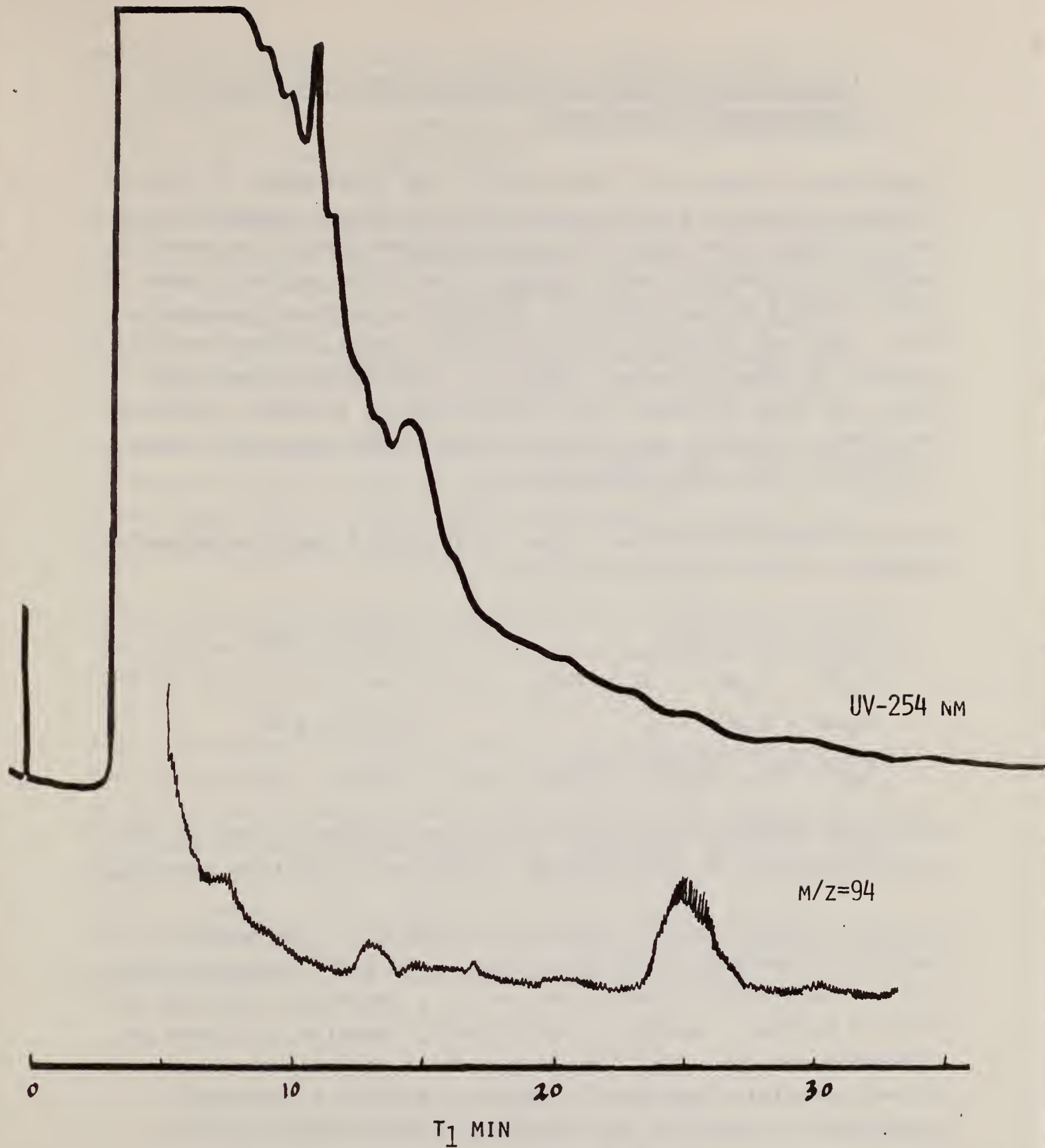
Figure 1. UV and MS chromatograms from direct HPLC injection of 1 microliter of shale oil containing 400 ppm of phenol.

1.e. Liquid Chromatograph with Electrochemical Detection of Organometallic Compounds

Significant progress has been made in the development of electro-chemical detectors for the measurement of trace organometallics. Past work has shown that the best detection limits for reducible analytes are obtained only through a laborious approach where the entire liquid chromatograph is enclosed in an inert atmosphere box. This was necessary to exclude all oxygen, which contributes greatly to detector noise. However, a new detector described below has been developed that allows work in a normal laboratory environment without sacrificing the excellent detection limits obtained in the inert atmosphere.

The new detection approach takes advantage of the electrochemical behavior of the organotin cations:

$$R_3Sn^+ + e \rightleftarrows R_3Sn\cdot \qquad\qquad E_{\frac{1}{2}} \approx -1.1 \text{ V}$$

$$R_3Sn\cdot + R_3Sn\cdot \rightarrow R_3Sn\text{-}SnR_3$$

$$R_3Sn\cdot \rightleftarrows R_3Sn^+ + e \qquad\qquad E_{\frac{1}{2}} \approx -0.9 \text{ V}$$

$$R_3Sn\text{-}SnR_3 \rightarrow 2R_3Sn^+ + 2e$$
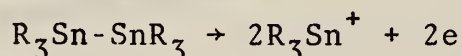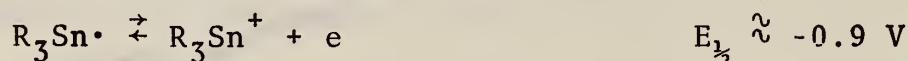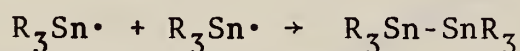
The first reduction step can lead to two products, both of which can be oxidized if the electrode is held at a positive potential.

The new detector cell is pictured in figure 2. The unique feature is the use of two electrodes: the first electrode that the L.C. effluent stream encounters is a generator electrode (G) that is held at a potential sufficiently negative to reduce the organotin cations. The flow then carries the products to a second detector electrode (D) which is held at a potential appropriate to oxidize the products. The advantage of this approach is that D can be poised at a potential where there is no response for oxygen; thus, the background residual current and noise are quite small. It is, however, prudent to remove

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most of the oxygen from the solvent by simple purging of the solvent reservoir, since the hydrogen peroxide formed on the oxygen reduction could chemically oxidize the reduced oxganotin products to an undetectable form.

Figure 3 shows a preliminary test of the new G-D cell with an electrochemically well-behaved organic compound (anthroquinone). The signal-to-noise ratio improvement with the new detector (on left) compared to direct reduction (on right) is readily apparent. The efficiency for the conversion and detection of the analyte was estimated at 31 percent for anthroquinone.

Figure 4 shows the detection of trace amounts of three organotin cations with the G-D cell. Limits of detection in the submicro-molar range (10's of ppb) can be anticipated, even for these difficultly reduced species.

Future work will evaluate the selectivity of this detector and investigate the advantages of the use of modulated waveforms to further increase the selectivity.

A detailed report "Assessing the Environmental Impact of Fossil-Fuel Based Energy Sources: Measurement of Organometal Species in Biological and Water Samples using Liquid Chromatography with Electrochemical Detection" (by W. A. MacCrehan and R. A. Durst, Center for Analytical Chemistry, NBS) was issued as EPA-600/7-79-211 (November 1979). This was an Interagency Energy/ Environment R&D Program Report with the cover title: Assessing the Environmental Impact of Fossil-Fuel Based Energy Sources.
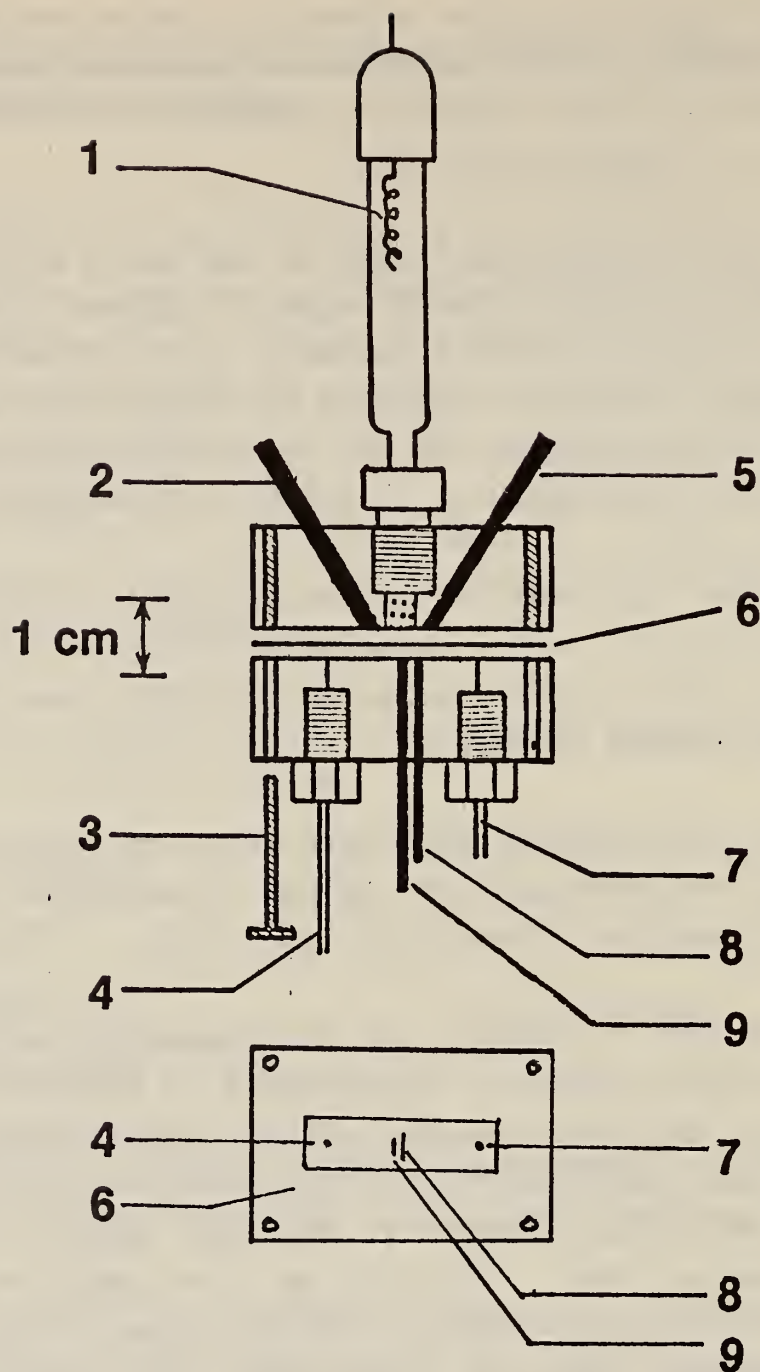
Figure 2. Generator-Detector (G-D) thin layer cell.

1 Reference electrode, 2 Auxiliary electrode (for detector), 3 Assembly screw, 4 Solution exit, 5 Auxiliary electrode (for generator), 6 Teflon spacer gasket, 7 Solution inlet, 8 Generator electrode (G), 9 Detector electrode (D).
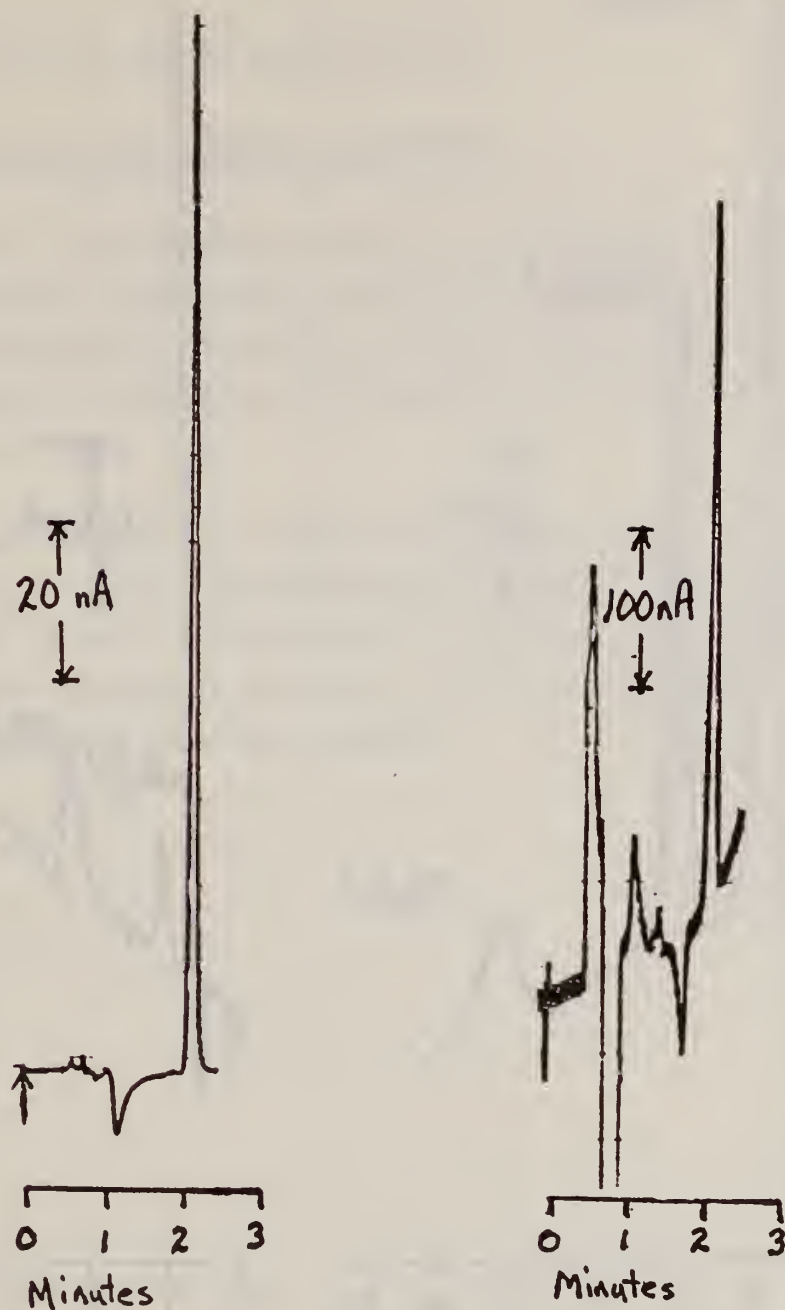
Figure 3. Comparison of G-D cell response to that of
a single electrode cell. Left chromatogram:
G @ -0.7V D @ +0.1V; right chromatogram
D @ -0.7V. Both are 20 µL samples of 10^{-4} mol/L
anthroquinone on Spherisorb ODS in 56% CH_3CN,
0.17 mol/L NH_4OAc @ 1.0 mL/min.

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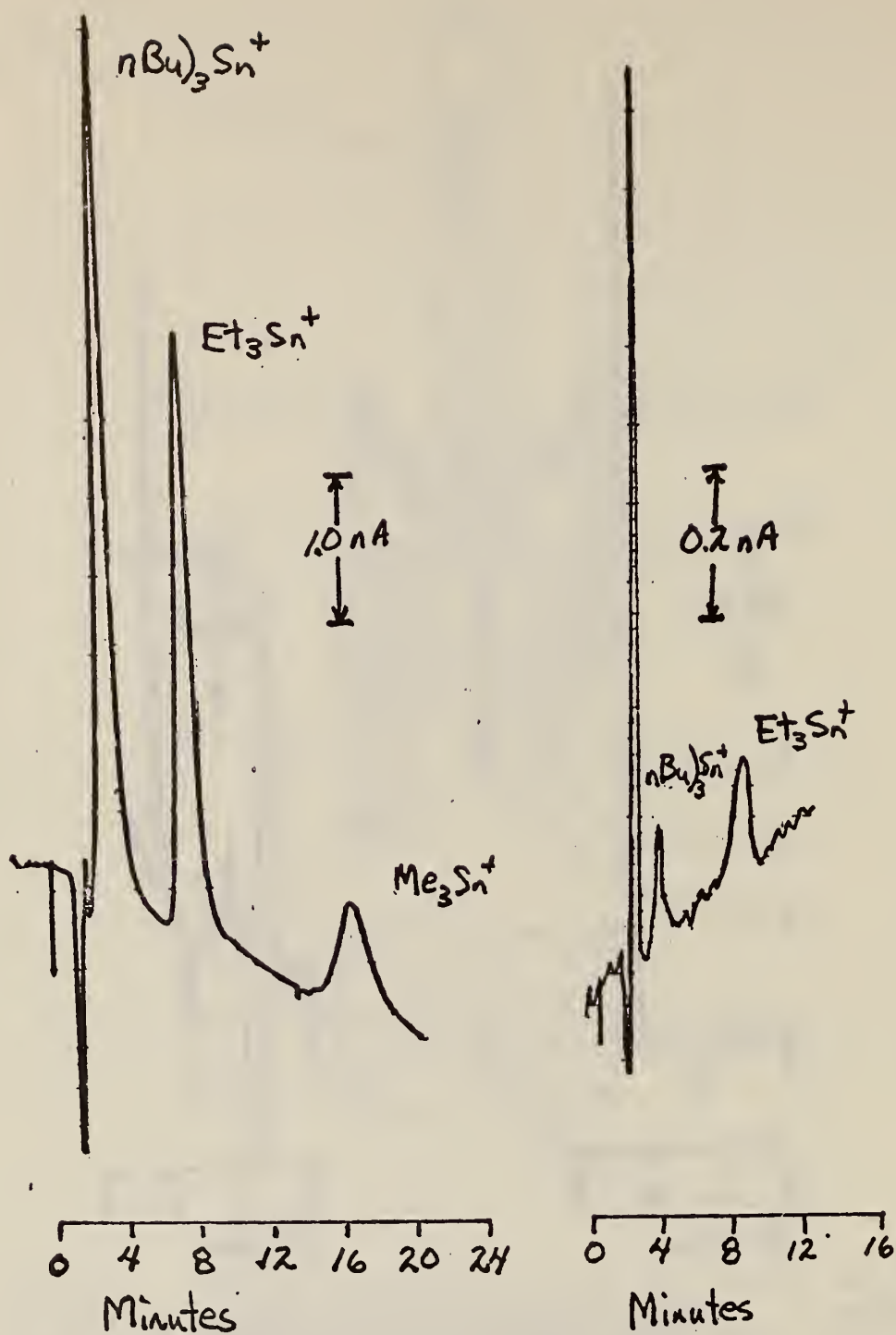
Figure 4. Detection of organotin cations with G-D cell.
G @ -1.2V, D @ +0.1V. Left chromatogram:
1×10^{-4} mol/L (approx. 30 ppm) of each; right
chromatogram: 2×10^{-6} mol/L (approx. 600 ppb)
of $nBu)_3Sn^+$, 3×10^{-6} mol/L (approx. 900 ppb) of
Et_3Sn^+.

1.f.   Laser Enhanced Ionization

A detailed report is under preparation.

1.g.   Speciation of Inorganic Pollutants

Development of a measurement method to distinguish forms (specia-
tion) of inorganic pollutants associated with energy related
effluents is necessary in order to assess the transport, trans-
formation, and distribution of inorganic pollutants in the
aquatic environment.

Preliminary experiments in separation techniques, in particular
high performance liquid chromatography (HPLC), and metal specific
detectors have shown a high degree of promise for speciation.
Based upon this approach, work will be initiated to develop
methods for chromium and tin species.

1. Development of Measurement Methods for Non-Volatile Organic Pollutants in Water Due to Energy Technologies

1.a. Raman Microprobe Characterization of Trace Polynuclear Aromatic Hydrocarbons

The analytical goals pursued in this work fall along two lines:

1) The development of Raman microprobe techniques to permit the analysis of microscopic volumes of effluents in liquid chromatography separations. The aim is to isolate sub-nanoliter fractions of the chromatographic effluent stream, and to determine the identity and concentration of the dissolved analyte(s).

Various approaches are being explored to render practical micro-Raman detection with LC separation techniques. These involve (i) trapping and isolation of effluent sampling volumes on sapphire substrates or by adsorption onto high-surface area, fine particulate solids (e.g., alumina); or, alternatively, (ii) isolation of the effluent in a microcapillary cell followed by analysis of the liquid sampling volume.

The latter method appears to offer the most straightforward approach. The Raman microprobe of present design permits the efficient excitation/collection of Raman scattered light from liquids confined to microcapillaries of 50 micrometers inside diameter. Ongoing work seeks to define the limits of detection for several of the common polynuclear aromatic hydrocarbons (PAHs) present at low concentrations in the usual liquid chromatographic solvents.

2) The Raman spectroscopic analysis of single particles of mass in the sub-nanogram range to characterize and identify the molecular forms and structures of the predominant inorganic and organic compounds present in such samples.

This work entails the acquisition of a library of micro-Raman reference spectra of environmentally significant chemical species, including, among others, those containing the elements sulfur, lead, vanadium, nickel, as well as inorganic and organic carbon. In the speciation of carbon compounds, the detection and identification of solid-phase hydrocarbons is of particular interest, especially with reference to their association with airborne particulate material.

Work in progress centers on the acquisition and interpretation of vibrational Raman spectra of laboratory-prepared samples, and of unknown particulate samples collected from sources associated with energy production and environmental degradation. Examples are the spectroscopic characterization of polynuclear aromatic hydrocarbons (PAHs) adsorbed as surface layers on inorganic microparticles (i.e., alumina) and the analysis of particulates produced in the combustion of fuel oils used in power generation.

1.b. Development of Specific Immunoassays for Dinitrophenols
      in Water

Work has focused on purification of specific antibodies required for production of accumulator columns that have adequate affinity for the ligand to which the antibodies were made. Continued efforts to optimize small molecule immunoassay with titrated antigens have not been fruitful; the binding is still low and thus the precision is not adequate for reproducible assays.

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It was postulated that significant non-specific binding reactions could be minimized by fractionation of the rabbit sera to obtain pure immunoglobulin (IgG) fractions. This has not been the case, although relatively pure IgG fractions were prepared by ammonium sulfate fractionation, gel-filtration, and ion-exchange chromatography. Affinity column purification of this purified material has not been successful, possibly due to the low amounts of IgG protein available for the columns.

The majority of the reagents for labeling the antibodies with ^{125}I have been obtained. We are presently identifying sources for gamma counting and for data reduction. Other options include labeling with fluorescein isothiocyanate or DTAF (5-[4,6-dichlorotriazin-2-yl-amino]fluorescein hydrochloride) to provide the basis for fluoroimmunoassay using photon-counting.

Finally, procedures have been selected for optimal coupling of antibodies to solid phase support beads in anticipation of more antibodies from rabbits that will be immunized with dinitrophenylated albumins over a longer time course than the previously immunized rabbits.

1.   Development of SRM's for Stationary Sources Associated with
      Energy Production

1.a. NO_2 in Air Gas Blend SRM's

The four levels of gas mixtures, 250, 500, 1000 and 2500 ppm NO_2
in air, have been received and each batch has been evaluated to
determine homogeneity. The batches at 250 and 2500 ppm were
produced by one supplier and the batches at 500 and 1000 ppm
were provided by another supplier.

The results of the first set of intercomparisons are given in
Table 3.

Table 3

Intercomparisons of NO_2 in Air Cylinders for Certification

Nominal Concentration (ppm)	Range of Concentration (ppm)	s.d. of the Concentration (ppm)
250	17	5
500	18	5
1000	12	3
2500	45	12

The lesser standard deviation relative to the range of values
reflects the fact that most samples had concentrations close to
the average but that in each lot there were several outliers. A
second analysis of all samples is essential to determine whether
the outliers represent unstable samples or samples whose concen-
tration fell at a lesser value at the time of preparation.

The results are encouraging, however, since a larger spread in the values was expected. A second analysis of the four sets is scheduled to start during the first week of April 1980.

1.b. SO_2 in N_2 SRM

Orders have been prepared for the purchase of 50 and 90 ppm SO_2 in N_2. The laboratory standards necessary for the certification of the 50 and 90 ppm SO_2 SRM's are being prepared and evaluated. Both a chemical method (hydrogen peroxide method) and gas chromatography will be used in the certification.

1.c. NO in N_2 SRM

No further work has been done since the issuance of the 1500 and 3000 ppm NO in N_2 SRM's.

1.d. O_2 in N_2 SRM's

Two new SRM's (SRM # 2657 and 2658) consisting of two and ten mole percent O_2 in N_2 have been completed. The material has been turned over to the NBS Office of Standard Reference Materials (OSRM) and the certificates are in preparation.

1.e. Stationary Source Gas SRM's

The anticipated time of completion of the final report on this phase of the program is June 30, 1980.

2. Development of SRM's for the Monitoring of Ambient Air Impacted by Emissions Resulting from Energy Production

2.a. Trace Level Reactive Gas SRM's

No report issued for this report period.

2.b. CO_2 in Air

Work on a set of 14 gravimetric standards has been completed.
The estimated uncertainty based on all recognized sources of
error does not exceed ± 0.1 percent relative (0.3 ppm) and is
probably somewhat less. Work is continuing to define this
error more absolutely.

Secondary standards for certification of SRM's have been
prepared and are being compared to the gravimetric standard.
An additional uncertainty due to the comparison process of
about ± 0.06 ppm will be assigned to the values of the concen-
tration of the secondary standards.

2.c.   Automation of Gas Analysis

A second Computer-Operated Gas Analysis System (COGAS-II) has
been constructed, and is in use for certification analyses of
SRM's.

A third system (COGAS-III) has been constructed. This system is
intended for the automation of permeation tube calibrations, and
preliminary results indicate that the system will operate as
intended.

2.d.   Development of a Traceability Procedure for Gas Standards

Preliminary reviews of a procedure for establishing traceability
of commercially prepared mixtures to certain gaseous SRM's have
been completed. A meeting with representatives of the gas
industry is planned for March, 1980 at which time the industry
will comment on the practicability of the procedure relative to
the state-of-the-art both of the preparatory processes and the
analytical procedures.

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3. Develop Methods for Dispersal of Particulates on Filter Media and Methods for Determining and Controlling the Composition and Morphology of Such Dispersed Particulates

3.a. Thin Glass Films Produced by Focused-ion Beam Sputtering

Since the last report we have compiled our completed work to date in a comprehensive report (now in press). This report includes our most recent work on the preparation of thin films from glass targets prepared at NBS that contain elements of low atomic number, such as sulfur and phosphorous. Plans for the remainder of this year include fabrication of several glass targets (18 cm diameter), each containing elements of interest to EPA. The proposed compositions of these targets are summarized in Table 4.

Table 4

Nominal Composition of Proposed Glass Targets (A-C) for 1980
(Percent Composition)

Compound	A	B	C
SiO_2	40	40	40
Al_2O_3	10	--	10
Fe_2O_3	10	--	--
V_2O_5	5	--	--
CaO	10	--	10
PbO	20	20	20
B_2O_3	5	--	10
TiO_2	--	10	--
ZnO	--	10	--
MnO_2	--	10	--
K_2O	--	10	--
Cr_2O_3			5
CuO_2			5

These glass targets will be fabricated and characterized by NBS. Several sets of films will then be prepared and characterized by x-ray spectrometry and/or other instrumental techniques. Several sets of characterized films will then be made available to EPA for their use.

4. Particulate Physical and Chemical Characterization

4.a. Particle Doppler Shift Spectrometer (PDSS)

As indicated in the preceding report, a vacuum sample tube was designed and installed in the PDSS in order to extend particle size measurements into the submicron range. Although the vacuum requirements are not extreme (down to a few torr), the stability of the system in holding a vacuum is critical due to the dependence of the slip correction and mean free path upon pressure. Extensive leak testing has been completed during which several components of the system (a pressure gauge and two high vacuum valves) were found to be defective and were replaced. The system is now ready to begin measurements of the slip correction and very low Reynolds number air flow phenomena, and of submicron aerosols.

Experimental studies of the extremely small particle-induced fluid flow phenomena (fluid flows of the order of 0.01 cm/s) have been completed, and a theoretical model has been developed through the exact solution of the Navier-Stokes equation in the low Reynolds number regime. The theoretical model agrees well with the experimental results. These studies are now being prepared for publication.

The PDSS has been used to help characterize the properties of several aerosol generators. Our experience with the spinning disk generator shows it to be useful for generating mono-dispersed dioctylphthalate aerosols in the size range greater than about 15

micrometers, but not as useful as the Berglund-Lui vibrating orifice generator in the less-than 15 micrometer range.

Studies have also been made on the properties of ammonium fluorescein for use as an aerosol material. Aerosols generated by the vibrating orifice from a solution of ammonium fluorescein are solid, spherical particles, and have optical properties that allow ready detection at trace levels by spectrophotometric techniques. They have very low volatility and a high melting point, making them suitable for electron microprobe and x-ray analysis. In addition, ammonium fluorescein is considered to be non-toxic. Measurement of the diameter of ammonium fluorescein particles generated using the vibrating orifice generator has demonstrated that the size of the aerosol can be predicted and controlled by the molarity of the fluorescein solution used in the generator.

5.   Particulates on Glass Fiber Filters

5.a.   Certification of SRM's for Pb, Sulfate, and Nitrate on Filter Media

Final certification of SRM 2673, Sulfate and Nitrate on Filter Media, and SRM 2674, Lead on Filter Media, has been completed. These materials are intended for use in the evaluation of apparatus and methods used in the determination of lead, sulfate, or nitrate in atmospheric particulates collected on filters.

Certification measurements for the anions were accomplished by ion chromatography. Lead for SRM 2674 was determined by both voltammetry and atomic absorption spectrometry (AAS). Statistical analysis of the data indicated no significant effects of biases in the AAS due to undissolved solids from the glass filter matrix.

Copies of the certificates of analysis are included for information.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 2673

Sulfate and Nitrate on Filter Media

This Standard Reference Material is intended for use in the evaluation of apparatus and methods used in the determination of atmospheric particulate sulfate and nitrate which have been collected on filters. It consists of a series of filter strips upon which sulfate and nitrate have been deposited in an essentially central location. The values certified correspond to the quantities of the substances leached from the filter strip without destruction of the filter matrix.

Sample Number	Sulfate content μg/filter		Nitrate content μg/filter	
	Average value	Tolerance limits	Average value	Tolerance limits
I	503	493 - 513	100	98 - 102
II	2002	1955 - 2049	1002	978 - 1026
III	6939	6635 - 7243	2513	2404 - 2622
Blank	2	0 - 6*	2	0 - 3*

* Range of measured values

The average value is the mean based on the analysis of 24 or 28 filters randomly selected from the lot. The tolerance limits are determined so that at the 95% confidence level they will contain the central 95% of the population of filter values. Details of the preparation, analysis, and statistical treatment of the data are given on the reverse side of the certificate.

This Standard Reference Material was prepared by B. I. Diamondstone. The analytical measurements were made by W. F. Koch. Statistical analysis of the data was provided by J. Orban. The overall direction and coordination of the preparation and analytical measurements leading to certification were performed in the Center for Analytical Chemistry under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
June 25, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

Preparation

This SRM consists of strips cut from glass fiber filters, such as are commonly used for measurements of atmospheric particulates, using high volume samplers. Solutions containing known amounts of potassium sulfate and potassium nitrate were prepared, gravimetrically, and multiple aliquots of 25 μL were placed on the filter strips. Four aliquots were so transferred to each filter in the case of samples I and II, and five in the case of Sample III. The pipets were calibrated by weighing similar aliquots transferred into weighing bottles.

The filters were prepared in a clean room and allowed to air-dry before packaging in glassine envelopes. The filters were prepared in groups of 100 and the proper number of aliquots were dispensed into weighing bottles at the beginning and end of each sequence, to monitor the performance of the pipet.

Analytical Measurements

Twenty four samples were randomly selected from the production lot (28 in the case of sample III) for chemical measurement of their extractable sulfate and nitrate. Each filter strip was extracted with a standard eluent (see below) for 15 minutes in a 55 °C ultrasonic bath. The extracts were analyzed for sulfate and nitrate by ion chromatography. The eluent was a solution of 0.003 M $NaHCO_3$ and 0.0018 M Na_2CO_3. A 100 μL sample loop was used. Peak heights were compared with those obtained from accurately prepared standard solutions. Three standards were prepared for each concentration level so as to bracket the extracts.

The randomly selected filters were also analyzed in random order. No significant systematic errors were observed related to the order of preparation. Average values and the overall standard deviation, s_0, of individual measurements were calculated. This standard deviation includes measurement error and filter content error.

The standard deviation, s_f, due to filter content variability was computed from a sample of 12 or 14 weighed quantities delivered by the pipets during the preparation of the filters. The resulting tolerance interval for the sulfate/nitrate contents is of the form

$$\overline{X} \pm k \, s_f .$$

It is this tolerance interval that should be of greater interest to the participating laboratory since it gives practical bounds for the likely values of the sulfate or nitrate contents that might be found in a given filter.

The following table lists the values of s_0 and s_f for each set of filters. The measurement standard deviation, s_m, for NBS can be computed using the relation $s_0^2 = s_m^2 + s_f^2$

Set	Average (μg)	s_0	s_f
I SO$_4$	502.6	8.89	3.14
NO$_3$	100.3	2.56	.63
II SO$_4$	2001.7	29.30	14.88
NO$_3$	1001.7	15.92	7.44
III SO$_4$	6939.0	109.35	100.75
NO$_3$	2513.0	43.70	36.30

The average values calculated from the composition of the solutions and the quantitites delivered by the pipets are in general agreement with the analytical values. However, the values certified are those obtained by analysis.

Recommended Usage

The material is not homogeneously distributed on the filter; hence the sample must be used in its entirety for analysis. It is recommended that the filter be extracted at 55 °C in an ultrasonic bath, with water or other nonreactive solvents. The filter base should not be digested to put it into solution.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 2674

Lead on Filter Media

This Standard Reference Material is intended for use in the calibration of apparatus and the evaluation of methods used in the determination of atmospheric particulate lead which has been collected on filters. It consists of a series of filter strips upon which lead has been deposited in an essentially central location. The values certified correspond to the quantities of the substance leached from the filter strip without destruction of the filter matrix.

Sample No.	Lead Content, μg/filter	
	Average Value	Tolerance Limits
I	100	97 - 103
II	303	294 - 312
III	1505	1477 - 1533
Blank	1.4	0.7 - 2.1*

*Range of measured values

The average value is the mean based on the analysis of 26 or 28 filters randomly selected from the lot. The tolerance limits are determined so that at the 95% confidence level they will contain the central 95% of the population of filter values. Details of the preparation, analysis, and statistical treatment of the data are given on the reverse side of this certificate.

This Standard Reference Material was prepared by B. I. Diamondstone. The analytical measurements were made by E. J. Maienthal and M. S. Epstein of the Inorganic Analytical Research Division. Statistical analysis of the data was provided by J. Orban of the Statistical Engineering Division.

The overall direction and coordination of the preparation and analytical measurements leading to certification were performed in the Center for Analytical Chemistry under the charimanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by T. E. Gills.

Washington, D.C. 20234
December 18, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

Preparation

This SRM consists of strips cut from glass fiber filters of the type normally used in high volume samplers for the measurement of atmospheric particulates. Solutions containing known amounts of lead nitrate were prepared gravimetrically, and aliquots of 25 μL were placed on the filter strips using micropipets. Four aliquots were transferred to each filter in the case of samples I and II and five in the case of sample III. The pipets were calibrated by weighing similar aliquots transferred into weighing bottles.

The filters were prepared in a clean room and allowed to air-dry before packaging into glassine envelopes. The filters were prepared in groups of 100 and the proper number of aliquots were dispensed into weighing bottles at the beginning and end of each sequence, to monitor the performance of the pipet.

Analytical Measurements

Twenty-eight filters were randomly selected from the production lot (26 in the case of Sample I) for chemical measurement of extractable lead. Selected filters were extracted with dilute nitric acid, using ultrasonic vibration to assist in the extraction. After the nitric acid extraction, the filters were thoroughly rinsed with distilled water to ensure complete extraction. The extracts were quantitatively diluted and analyzed by linear sweep voltammetry which had been calibrated with solution standards prepared from high purity lead.

The selected filters were analyzed in random order. No significant systematic errors were observed related to order of preparation. Average values were calculated together with the overall standard deviation, s_o, of individual measurements. This standard deviation includes measurement error and filter content error. The resulting confidence interval for the mean is of the form

$$\overline{X} \pm t\, s_o/\sqrt{n},$$

where s_o is based on $n - 1 = 27$ degrees of freedom.

A selected number of filters were also analyzed by atomic absorption. The results obtained were well within the tolerance limits given and were consistent with the certified values.

The standard deviation, s_f, due to filter content variability was computed from a sample of 12 or 14 weighed quantities delivered by the pipets during the preparation of the filters. The resulting tolerance interval for the lead content is of the form

$$\overline{X} \pm k\, s_f.$$

It is the tolerance interval that should be of greater interest to the participating laboratory since it gives practical bounds for the likely values of the lead content that might be found in a given filter.

The following table lists the values of s_o and s_f for each set of filters. The measurement standard deviation, s_m, for NBS can be computed using the relation $s_o^2 = s_m^2 + s_f^2$

Set	Average (μg)	s_o	s_f
I	99.7	1.59	0.89
II	302.9	5.37	3.00
III	1505.2	12.73	9.24

The average values calculated from the composition of the solutions and the quantities delivered by the pipets are in general agreement with the analytical values. However, the values certified are those obtained by the analysis.

Recommended Usage

The material is not homogeneously distributed on the filter, hence the sample must be used in its entirety for analysis. It is recommended that the filter be extracted at 45-50°C in an ultrasonic bath, with dilute nitric acid (2 mL HNO_3 + 15 mL H_2O). After extraction the filters should be thoroughly rinsed with distilled water. The filter base should not be dissolved.

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6.   Urban Air Particulate, Washington, D. C. Sample

In August 1979, the collection of the Washington, DC, urban
particulate sample was terminated. The bags were vacuumed out
using the same system as that described for the St. Louis
material, and approximately 45 pounds of unsieved material was
obtained. Several sieving strategies were evaluated in order to
develop one that was effective in removing bag fibers, but did
not excessively reduce the non-bag fiber fraction of the sample.
It appears that 30-35 lb. of sieved material will be available
for final analysis. Preliminary inorganic, organic, and particle
size analysis has been performed on the Washington material. The
analysis indicated that the Washington material can be used either
as a replacement for the St. Louis material or as an organic
certified sample. A final decision regarding the Washington
material will be made toward the end of FY-80, after additional
information on the sales of SRM 1648 (St. Louis material) and the
preliminary organic analysis of the Washington material are
completed.

Some preliminary work has been performed on converting the bag-
house facility to a system to collect only respirable particulate
material. Discussions with various EPA laboratories indicated
that this was the highest priority need for further collection
studies. It is anticipated that these respirable particle
collection feasibility studies will be completed by the end of
fiscal year 1980.

7.   Develop SRM's for Coal Conversion Processes and Materials
     Balance Determinations

No report issued this report period.

8.   Development of an Oil Shale SRM

As previously reported, a quantity of Oil Shale SRM has been
sterilized and set aside for comparison with unsterilized Oil
Shale to determine if there are any changes in the concentration
of volatile substances, both organic and inorganic. However, a
period of prolonged down-time for the NBS reactor has delayed
further research on this material.

1. Development of an Instrument to Measure Airborne Sulfate
    Particulate Matter

Work has continued on the characterization and optimization of
the pulsed precipitator/flame photometric detector (FPD) aerosol
sulfate measurement technique. As indicated in the preceding
report, we made an evaluation of the feasibility of doping the
hydrogen gas with SO_2 or ethyl mercaptan in order to increase
the total FPD response into a range where the instrument is more
stable, and to increase the sensitivity of the response. The
sensitivity of the system is a function of the total signal,
because the FPD response (R) is nonlinear with sulfur concentra-
tion(s); (i.e., $R \propto [S]^n$, where n = 1.8, therefore Sens. = $\frac{dR}{d[S]} \propto$
$n[S]$). We have experimentally verified this prediction; viz., an
increase in total sulfur concentration of a factor of 2.6 is
predicted to give an increase in sensitivity of 4.7, in good
agreement with an observed increase of 5.1.

An important limitation in the application of the FPD for airborne
sulfate particulate measurement is the slow response time of the
burner to changes in sulfur concentration. The rise time for 90
percent of full equilibrium response is about 15 seconds, and
the fall time is 2.8 seconds. For a precipitator operating
frequency of 0.2 Hz we can obtain only 60 percent of the poten-
tially available response. This is equivalent to a loss in
sensitivity of almost 50 percent. We therefore have looked for
better burner designs. We recently evaluated a burner and
detector system built by Dr. Don Stedman at the University of
Michigan and found that it was much faster (rise time = 1 sec;
fall time = 0.2 seconds). We will obtain this instrument through
a collaborative study arrangement, evaluate the burner for
sensitivity, and optimize it for application with the pulsed

precipitator technique.   Table 5 shows a comparison of the
percent of full response vs. precipitator frequency for the
instrument we have been using, and for the University of
Michigan burner/detector.

Table 5

Recovery of Potentially Available Response vs. Precipitation
Frequency

| Frequency (hertz) | Percent of Full Response | |
	Meloy[a] FPD	U. of Mich. FPD
.2	60	100
.5	17	85
1.0	5	65
2.0	2	30
4.0	--	10

[a]In order to adequately describe materials and experimental
procedures, it is occasionally necessary to identify commercial
products by manufacturer's name or label.   In no instance does
such identification imply endorsement by the National Bureau of
Standards nor does it imply that the particular products or
equipment is necessarily the best available for that purpose.

80-BCL-c-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Radiocarbon as an Environmental Trace

1.a. Applications

The use of miniradiocarbon measurements with 5-10 mg (carbon)
environmental samples (gases, atmospheric particles, sediment)
has continued with the objective of utilizing the natural $^{14}C/^{12}C$
ratios to distinguish between biogenic and fossil pollutant
sources. Important progress has been made in our understanding
of the source of carbonaceous particles, especially of those
collected in urban areas, through several cooperative studies
with industry* and universities**. A critical element in these
investigations has been the utilization of sample selectivity
(chemical and physical) in combination with the radiocarbon
measurements. That is, because small samples can be used, we
have been able to increase the "information content" of our
measurements by examining samples that have been preselected
according to geographical region, known activities, chemical
nature, and stable isotopic composition. A summary of our
recent radiocarbon results, together with an indication of these
critical supporting data, is given in figure 5. The general
conclusions to be drawn from these studies are (i) urban particles
tend to show predominately fossil carbon (though with a non-
negligible biospheric contribution); and (ii) particles from
remote locations contain less organic carbon, which is primarily
biogenic. An extremely important exception occurred in the

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* General Motors, Global Geochemistry Corporation.
** Oregon Graduate Center, Colorado School of Mines, University
of Washington.

RADIOCARBON IN AEROSOLS AND SEDIMENT

	Mass-Carbon (mg)	% Contemporary [$^{14}C/^{12}C$] (± one standard deviation)	Supporting Data
Ambient Particles			
Los Angeles	7.8	23 ± 15	Organic (insoluble)
Salt Lake City	5.3	28 ± 13	Composition
Utah Desert	10.2	88 ± 16	
Impact Particles (<3 μm)			
Portland, OR.	5.1-10.7	62. – 107.	Inorganic Composition
Sediment			
Puget Sound, WA. FA	60.	86 ± 21	Isotopic ($^{13}C/^{12}C$)
PAH	14.	19 ± 21	Composition

(FA = Fatty acid fraction, PAH = Polycyclic Aromatic Hydrocarbon fraction).

Figure 5.   Percent of contemporary (biogenic) carbon deduced from radiocarbon measurements on small (∿ 10 mg) environmental samples. Supporting inorganic, organic, and isotopic (^{13}C) data aided in source resolution/confirmation. References: Ambient Particles (Currie et al., 1978); Impact Particles (Cooper, Currie, and Klouda, 1979b), Sediment (Swanson, Fairhall, and Currie, 1979).

Portland Study***, where the combustion of biospheric material (field, slash, and residential wood burning) led to the first observations of urban carbonaceous particles containing up to 100 percent biogenic carbon. These results have caused us to focus on the air pollution potential of residential wood combustion — a problem which will be a subject of our continuing studies (see figure 6).

1.b. Research Advances

Research activities have been directed toward the analysis of atmospheric gases, high accuracy natural radiocarbon measurements, chemical-mathematical investigations of the Radiocarbon Dating Calibration Curve, and extension of the state of the environmental radiocarbon art to microgram samples using Accelerator Mass Spectrometry. Work with the atmospheric gases is still in the initial stages; thus far milligram quantities of atmospheric methane**** have been extracted for radiocarbon measurement. High accuracy radiocarbon measurements are underway in connection with calibration of the new NBS International Radiocarbon Dating Standard, and concomitant chemical-statistical investigations have been performed in cooperation with the Australian National University on an International Laboratory Intercalibration exercise involving some 20 laboratories and three calibration materials (Oxalic Acid, 1850 Tree Rings, Sucrose). Evaluation of the fluctuations of the Radiocarbon Dating Calibration Curve is underway in cooperation with the Statistical Engineering Division

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*** The Portland Aerosol Characterization Study measurements were carried out in cooperation with the Oregon Graduate Center and the Oregon Department of Environmental Quality.

**** The methane study, of interest for climatic reasons and to learn about man's perturbation of the carbon cycle, is being carried out in cooperation with NOAA (Air Reserves Lab).

WOOD BURNING

Utilization

- **Scandinavia:** Finland projects 30% (by end of 1980's); Sweden, 58% (by 2015)

- **U.S.:** A major fuel, ranks with hydroelectric and nuclear (wood stove sales: 10^6/yr.)

Environmental Significance

- **Particle emissions:** 20–50 times oil, gas/Btu, primarily fines (respirable)

- **Incomplete combustion→soot, PAH, HCHO, phenols, . . .**

Observed Impacts

- **Bangor, ME:** 8 $\mu g/m^3$ (inventory)
- **Portland, OR:** 24 $\mu g/m^3$ (radiocarbon)

Figure 6. Wood as a fuel: Utilization and particulate pollution. Information on wood utilization may be found in Brooke (1979) and Trefil (1978); on environmental significance and impacts, in Cooper, Currie, and Klouda (1979a) and Butcher (1978).

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of NBS under the auspices of an international committee formed for this purpose. Information to be derived includes the assessment of accuracy, development of an accepted calibration curve for accurate dating, and geophysical model information for the assessment of past climatic variations (figure 7). Studies initiated in 1979 show outstanding promise for the analysis of extremely "old" and extremely small samples. Our exploratory work, which utilized the NBS variable geometry isotope separator and the University of Rochester Tandem Van de Graaff Accelerator, demonstrated the feasibility of measuring natural radiocarbon in the 10 µg range. All of the above activities are intended to increase our ability to extract reliable information on anthropogenic and natural contributions to both environmental pollutants and chemically-induced climatic perturbations, now and in the past.

2. Organics on Air Particulates

In a previous report (FY-78) we described analytical methods for the isolation, separation, and identification of polycyclic aromatic hydrocarbons (PAH) in urban air particulate matter. These methods have been employed for the qualitative characterization of the PAHs on SRM 1648 (Urban Air Particulate Matter).

An important part of this methodology is the use of normal phase high-performance liquid chromatography (HPLC) on an aminosilane column to isolate PAH fractions according to the number of condensed aromatic rings [Anal. Chem. 49, 2306 (1977)]. The normal phase liquid chromatogram of the analysis of the urban air particulates (SRM 1648) is shown in figure 8. Each of the numbered fractions was then analyzed by gas chromatography/mass spectrometry (GC/MS) and reverse-phase HPLC with fluorescence detection for identification of the PAH. The GC analyses of fractions 3, 4, and 5 are shown in figure 9. The isolation of PAH fractions in this manner allows identification of many

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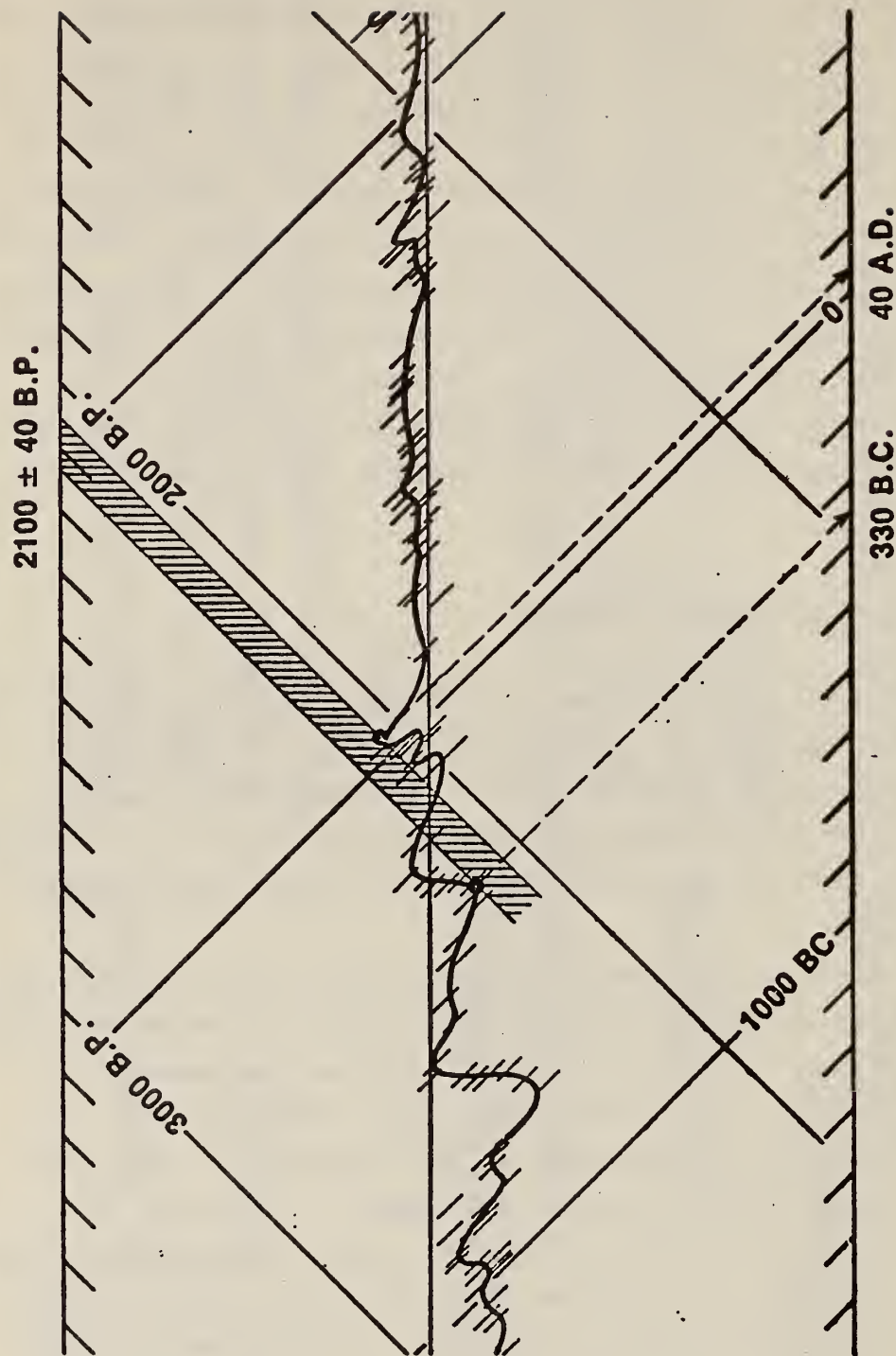
Figure 7. Magnification of age uncertainty interval of a dated wood sample because of natural radiocarbon variations. (The underlying radiocarbon calibration curve has been adapted from [Suess, 1970] by permission of Alquist and Wiksell Förlag AB).

Urban Air Particulates - Normal Phase HPLC
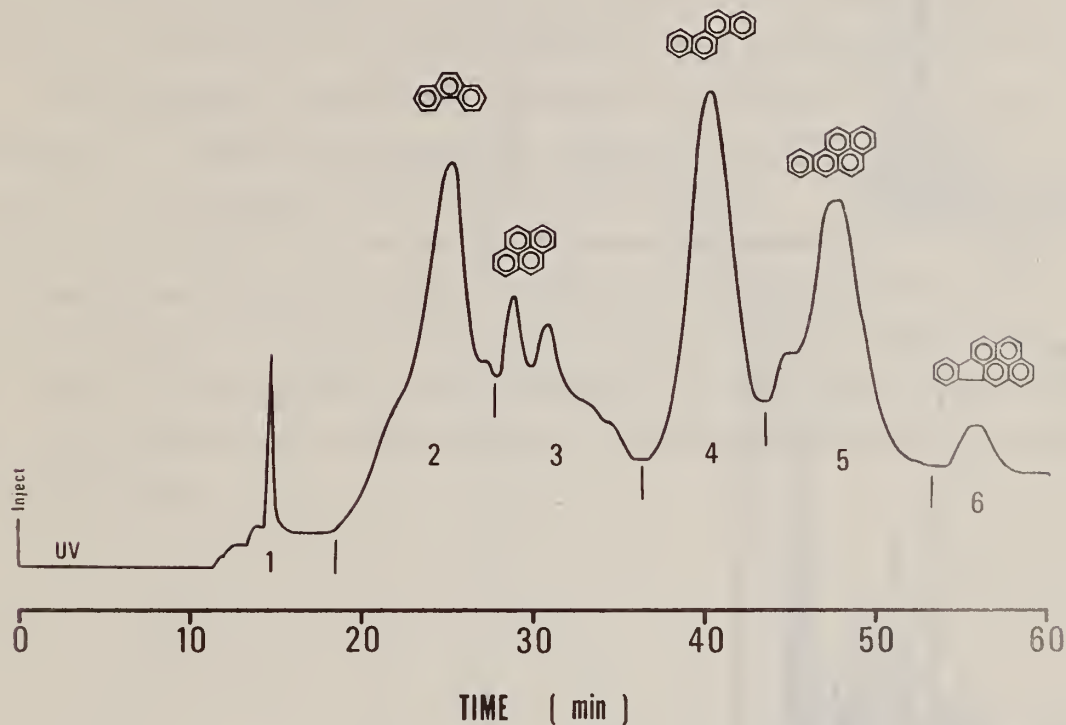
Figure 8. Normal phase liquid chromatogram of PAH extracted from urban air particulates. Column: semipreparative μBondapak NH₂. Detection: UV absorbance at 254 nm. Conditions: n-hexane at 1 mL/min. Numbers indicate fractions collected for subsequent analysis and the PAH structures indicate elution times for these representative compounds.

Fraction 5

Fraction 4
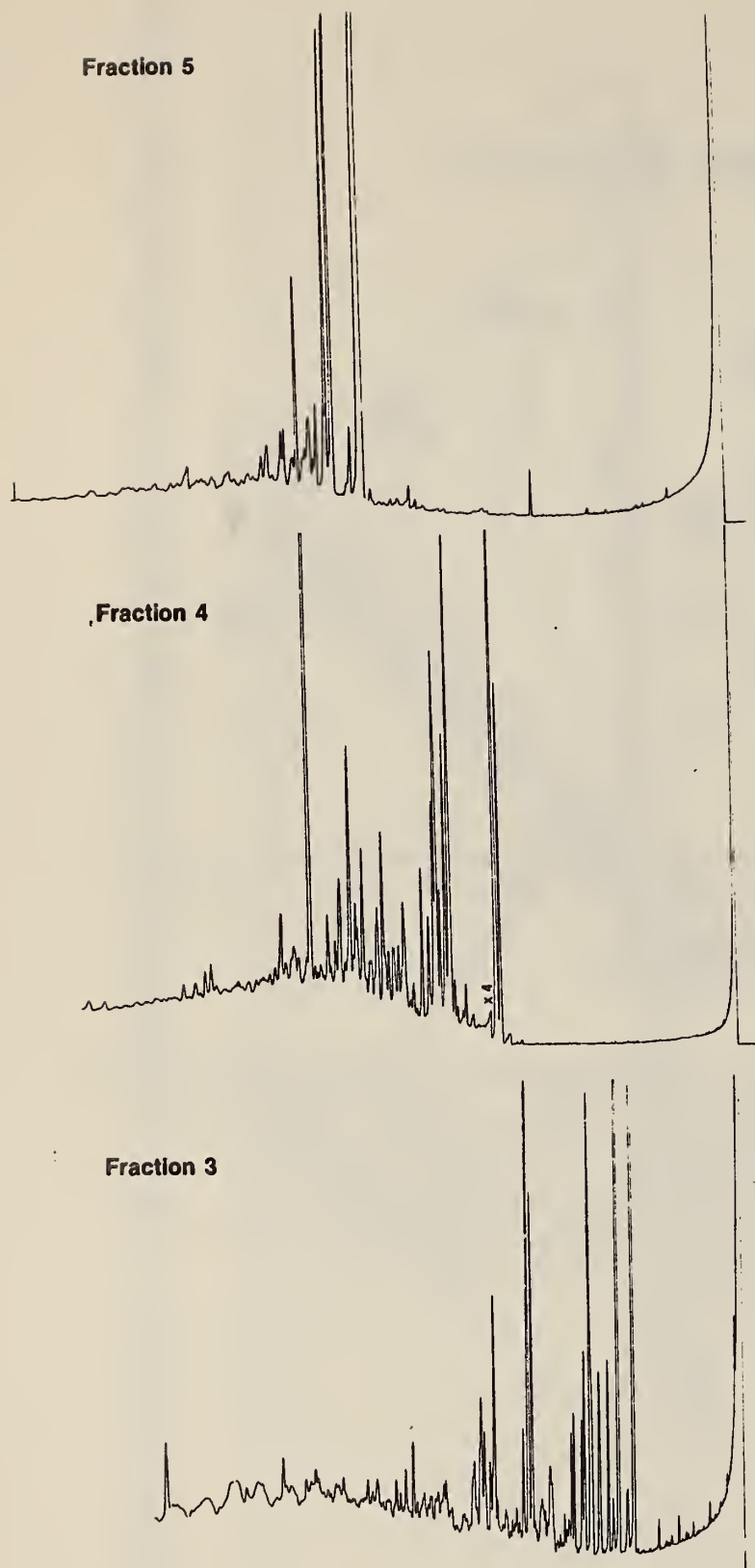
Fraction 3

Figure 9. Gas chromatograms
of fractions 3, 4,
and 5 from urban
air particulates.
(see figure 8)
Column: SE-54
WCOT glass capil-
lary, temperature
programmed from
200-270° at 2°/min.

minor components in the mixture which would otherwise be obscured. The PAHs identified in SRM 1648 are summarized in Table 6. Reverse-phase HPLC analyses of the fractions using fluorescence detection confirmed the identities of many of the PAHs. The liquid chromatogram of the analysis of fraction 4 is shown in figure 10.

Several different organic solvents have been investigated for ultrasonic extraction of the PAHs from the particulate matter (i.e., cyclohexane, methylene chloride, methanol, and tetra-hydrofuran). There are numerous reports in the literature of the use of cyclohexane for these extractions. In our studies the polar solvents appear to be more effective in removing the PAHs from these particulates. However, these solvents also remove additional organic compounds (i.e., those more polar than PAHs) which create additional problems in the isolation of the PAHs. The analytical methodology is being modified to solve these problems.

Table 6

PAH's Identified in Urban Air Particulate Matter (SRM 1648)[a]

Fraction 2

Phenanthrene[b]
Anthracene[b]
Methylphenanthrenes/anthracenes (4)
    (probably methylphenanthracenes)
4H-cyclopenta(def)phenanthrene
C_2-phenanthrenes/anthracenes (6)
Methyl-4H-cyclopenta(def)phenanthrene

Fraction 3

Fluoranthene[b]
Pyrene[b]
Methylfluoranthenes/pyrenes (5)
Benzo[a]fluorene
Benzo[b]fluorene
C_2-Fluoranthene/pyrenes (2)
Benzo[b]naphtho[2,1-d]thiophene
Benzo[c]phenanthrene
Benzo[ghi]fluoranthene
Cyclopenta[cd]pyrene
Benzacenaphthylene
Unknowns of molecular weight 230 and 234

Table 6 continued.

Fraction 4

    Benz[a]anthracene[b]
    Chrysene[b]
    Triphenylene[b]
    Methylbenz[a]anthracenes/chrysenes/triphenylenes (3)
        (1-methyl-, 2-methyl-, and 3-methylchrysene)[b]
    Binaphthyls (3)
    C_2-benz[a]anthracenes/chrysenes/triphenylenes (2)
    Methylbinaphthyls (3)
    Quarterphenyl
    Unknowns of molecular weight 240 and 278 (3)

Fraction 5

    Benzo[b]fluoranthene[b]
    Benzo[k]fluoranthene[b]
    Benzo[e]pyrene[b]
    Benzo[a]pyrene[b]
    Perylene[b]

Fraction 6

    Indeno[1,2,3-cd]pyrene[b]
    Benzo[ghi]perylene[b]

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[a] Identities of specific isomers based on mass spectra and gas chromatographic retention time.

[b] Identity confirmed by HPLC and fluorescence spectroscopy.

Urban Air Particulates - Fraction 4
Reverse Phase HPLC
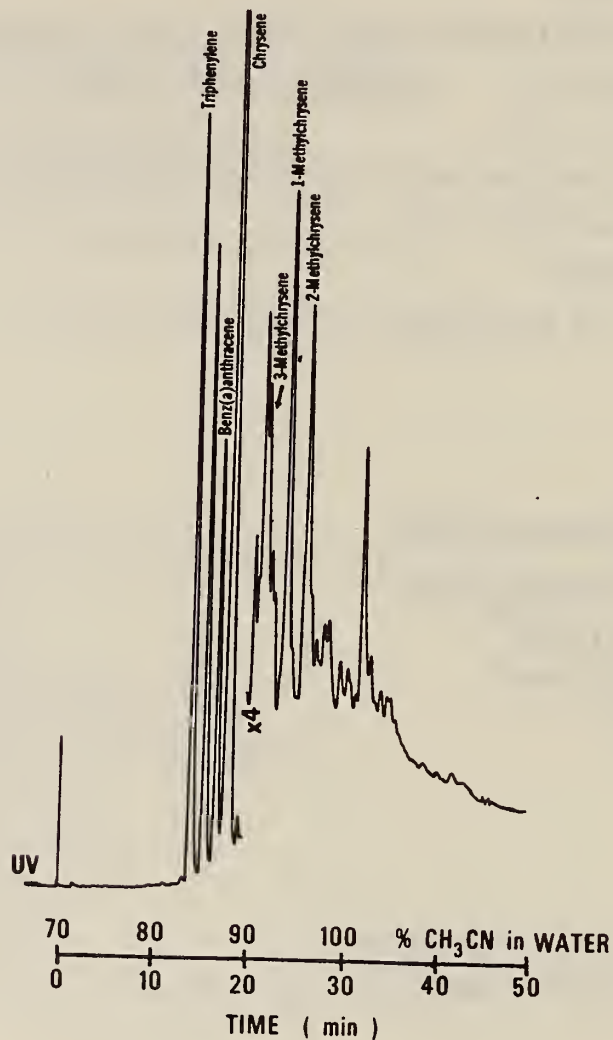
Figure 10. Reverse phase liquid chromatographic
analysis of fraction 4 from urban air
particulates (see figure 8).

Column: Vydac 201TP reverse phase.
Detection: UV absorbance at 254 nm.
Conditions: linear gradient from 70-100
percent acetonitrile in water at 1%/min
at 1 mL/min.

80-BCM-a-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Energy Related Water Pollutant Standard Reference Materials

1.a. Complete Certification of Ocean Sediment SRM

There has been no activity in this project during the reporting
period.

1.b. Complete Certification of SRM 1646, Estuarine Sediment

Certification analyses for SRM 1646, Estuarine Sediment, are
mostly complete. The residual analytical effort, statistical
analysis of the data and final certification are likely to occur
during the next reporting period.

1.c. Trace Elements in Water, SRM 1643

Statistical analysis of the trace element data for SRM 1643a
(re-issue) revealed the need for some additional study of
arsenic. Pending the completion of this work, final certifica-
tion and availability of the SRM are anticipated during the next
reporting period.

1.d. Aqueous Polynuclear Aromatic Hydrocarbon Standard SRM 1644

In previous reports, generator column technology was described
as an ideal technique for preparing saturated standard solutions
of individual polynuclear aromatic hydrocarbons (PAHs). Certi-
fication of generator column standards for benzo(a)pyrene,
benz(a)anthracene, and anthracene are in process.

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2. Matrix Isolated Laser Raman Identification of GC Effluents

A new, primary laboratory measurement technique is being developed for the analysis and certification of Standard Reference Materials and the performance of referee-type measurements of regulated trace organics in water. This new method involves laser Raman scattering from pollutants isolated in cryogenic matrices.

Over the past several months we have demonstrated the technical and scientific feasibilities of sequentially acquiring and analyzing complex mixtures of volatile organics such as those currently being regulated by the EPA. Our diagnosis, laser Raman spectroscopy of matrix isolated samples, should provide a molecular specificity and sensitivity comparable to, or better than, existing techniques utilized for water quality assessment. For example, in analyzing sample mixtures of isomeric species such as the dichloroethylenes, it has been demonstrated possible to correctly identify the mixture components even when one component was present in a large excess of another. In addition, scaling laws for quantification, such as signal dependence on laser power, sample concentration, deposition time, mixture purity, etc., have been extensively studied. Of significant note is the ability to qualitatively determine all components of even very complex mixtures by their characteristic Raman signatures. Inherent in the matrix-isolation technique is the independence of the signal from one component due to the presence or absence of other pollutant species in the same sample.

Our previous efforts have been concerned with laboratory samples and manual realignment of deposition source, new matrix sample, and spectrometer.

When fully automated, our GC-cryostat should provide the capability for quantitative analysis of real-world water samples. Our present efforts have been in upgrading our system to be used as an analytical tool. We have initiated procurement for a dedicated GC system for initial separation and sample acquisition; obtained plans for the modification of our existing cryostat to be compatible with automatic sample acquisition and analysis; and procured and interfaced a computer-controlled optical multi-channel analyzer (OMA) to decrease analysis time and to allow for spectral analysis, comparison to library stored references, and quantitation of signal strengths to give an accurate analysis of the purity of each successive water sample.

The GC under consideration is a capillary system with standard FID. It will be possible to modify this system to interface to the vacuum chamber of our cryostat. The GC effluent (i.e., separated pollutants in an excess of argon carrier) will enter the sampling chamber through capillary tubing and impinge on an octagonally-shaped gold-coated cold finger maintained at 14 °K. The sample will condense in an area of approximately 10^{-2} cm^2. The cold finger will be rotated about a screw axis by an external servo-control to present a new region for subsequent sample deposition; the previous sample being moved into the interrogation region for the Raman spectrometer. Each sample is analyzed as subsequent samples are acquired. The identity, composition, and concentration of each sample is recorded in the computer memory. The computer-controlled OMA allows for spectral acquisition in a few seconds that currently takes 10-30 minutes in our single channel system. There will be room for approximately 48 samples on the cold finger. These samples may either be obtained from subsequent (different) portions of the GC effluent of a single water sample extract, or a single cut, representing particular retention time windows from each of a number of different water sample organic components. When the cold finger

has been fully analyzed it is renewed by simply flash heating in vacuo and re-cooling—a process requiring 10-20 minutes. Up until the time of such a clean-up procedure any given sample locus can be re-examined under high resolution Raman, or for an extended period of time to test for very low levels of a given pollutant, or to clarify an analysis.

1.   Develop Organic SRM's for the Calibration of Energy-Related Water Pollutant Measurement Methods

1.a.   Coal Conversion

There has been no activity in this project during the reporting period.

1.b.   Analysis of Phenolic Species in Alternate Fuels and Effluents

As part of a project to certify a shale oil SRM and to develop methods for quantitating trace levels of important organic compounds, phenol and o-cresol concentrations in a shale oil have been determined by gas chromatography-mass spectrometry with selected ion monitoring. High performance liquid chromatographic fractionation of the shale oil on a semi-preparative scale aminosilane column was used to obtain a 'phenolic' fraction which was free from other interfering compounds in the shale oil matrix (the use of HPLC for the fractionation of shale oil has been described in previous reports). Additional specificity and enhanced precision were achieved with the use of selected ion monitoring (SIM) gas chromatography-mass spectrometry. Gas chromatographic separations were carried out on specially prepared wall-coated open-tubular columns coated with Pleuronic L-64. This liquid phase separates compounds based on their polarity, and provides excellent resolution of the C_1-C_4 substituted phenols detected in the shale oil (see figure 11). The superior resolution, along with the specificity of selected ion monitoring, allows accurate quantitation of phenols in a complex matrix such as the shale oil.

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A standard addition method was used for quantitation. The molecular ions for phenol (m/e 94), o-cresol (m/e 108), and m + p-cresol (m/e 108 monitored as a volume correction standard to compensate for variable injection volumes) were monitored in 0.1 amu increments (to insure that the voltage is sampled at the peak maximum); see figure 12. Peak areas for the analyte and the volume correction standard were integrated, and ratios of the analyte/volume correction standard plotted vs. the concentration of analyte added. The concentration of the analyte in the shale oil was then determined from the ordinate intercept (see figure 13). Nine standard addition experiments were run to test homogeneity of the shale oil sample. The results of these determinations, shown in Table 7, compared favorably with values determined independently by a gas chromatographic method.

Table 7

Phenol and O-cresol Concentrations in Shale Oil

Method:	GC/MS	GC
phenol =	407 ± 37 ppm[a] (n=9)	401 ± 9 ppm (n=8)
o-cresol =	382 ± 40 ppm (n-9)	384 ± 20 ppm (n=8)

[a]95 percent confidence limits (2σ).

1.c. Development of a Phenol in Water SRM

Determination of individual phenols in environmental samples is of particular interest because many substituted phenols have been found to be toxic to aquatic life. Phenols are present in a wide variety of chemical processes, either as end products or as intermediates. It has therefore been necessary to develop an analytical procedure for the determination of phenols in water.

To date, a literature search has been made to obtain pertinent information on the characteristic behavior of phenols in water.
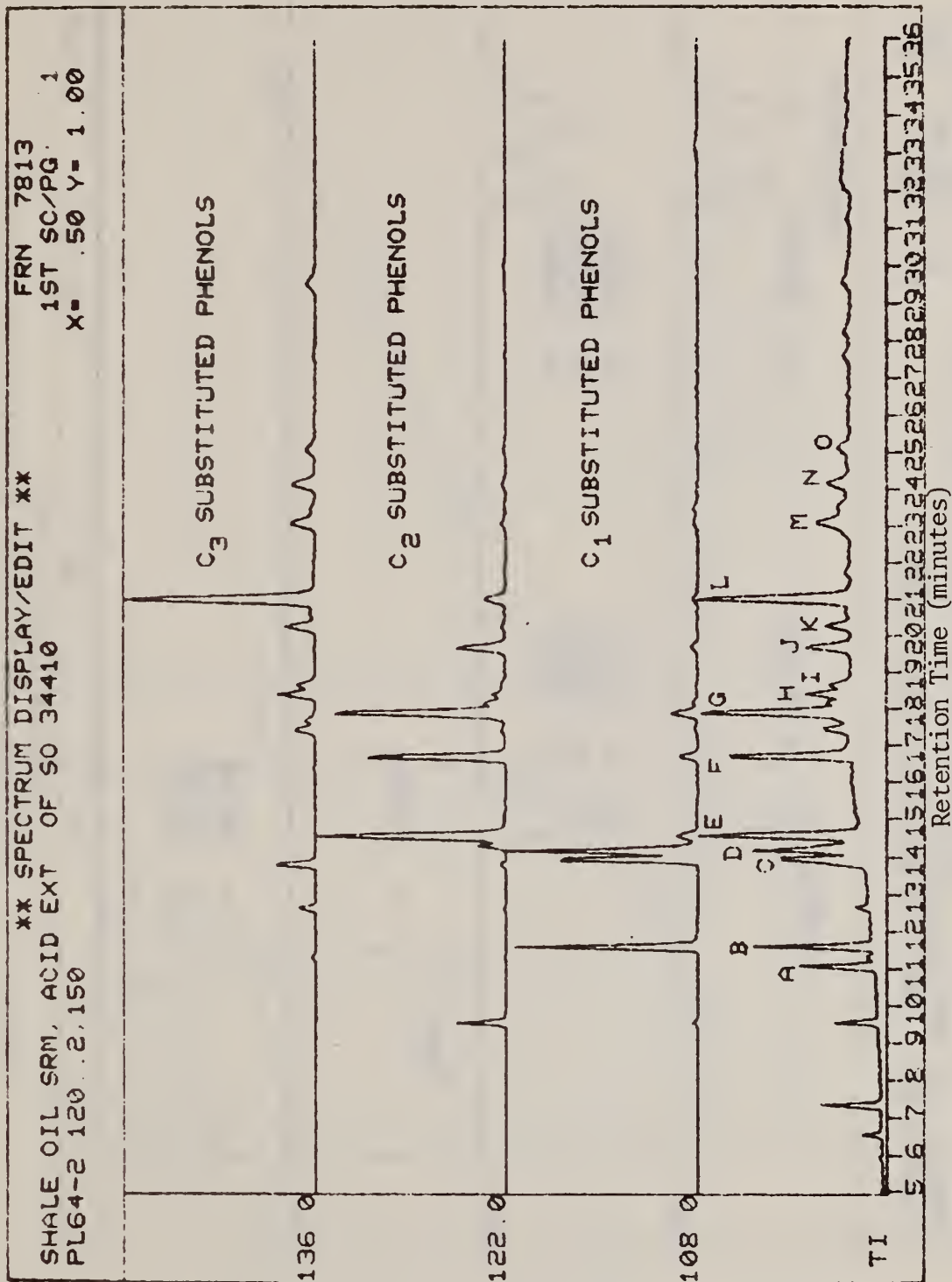
Figure 11. Acid extract of shale oil chromatographed on 20 m PL-64 column.

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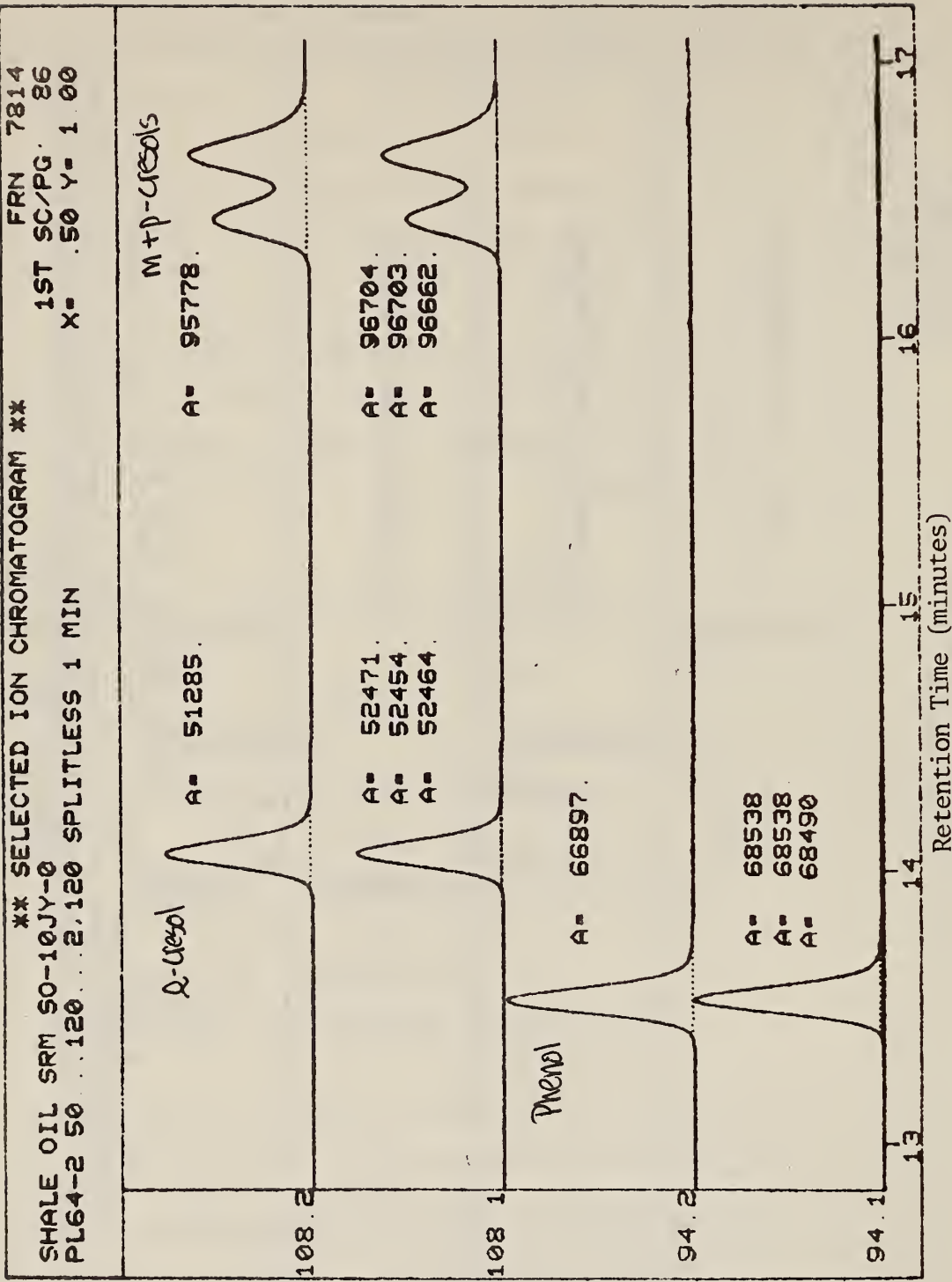
Figure 12. SIM analysis of HPLC fractionated shale oil.
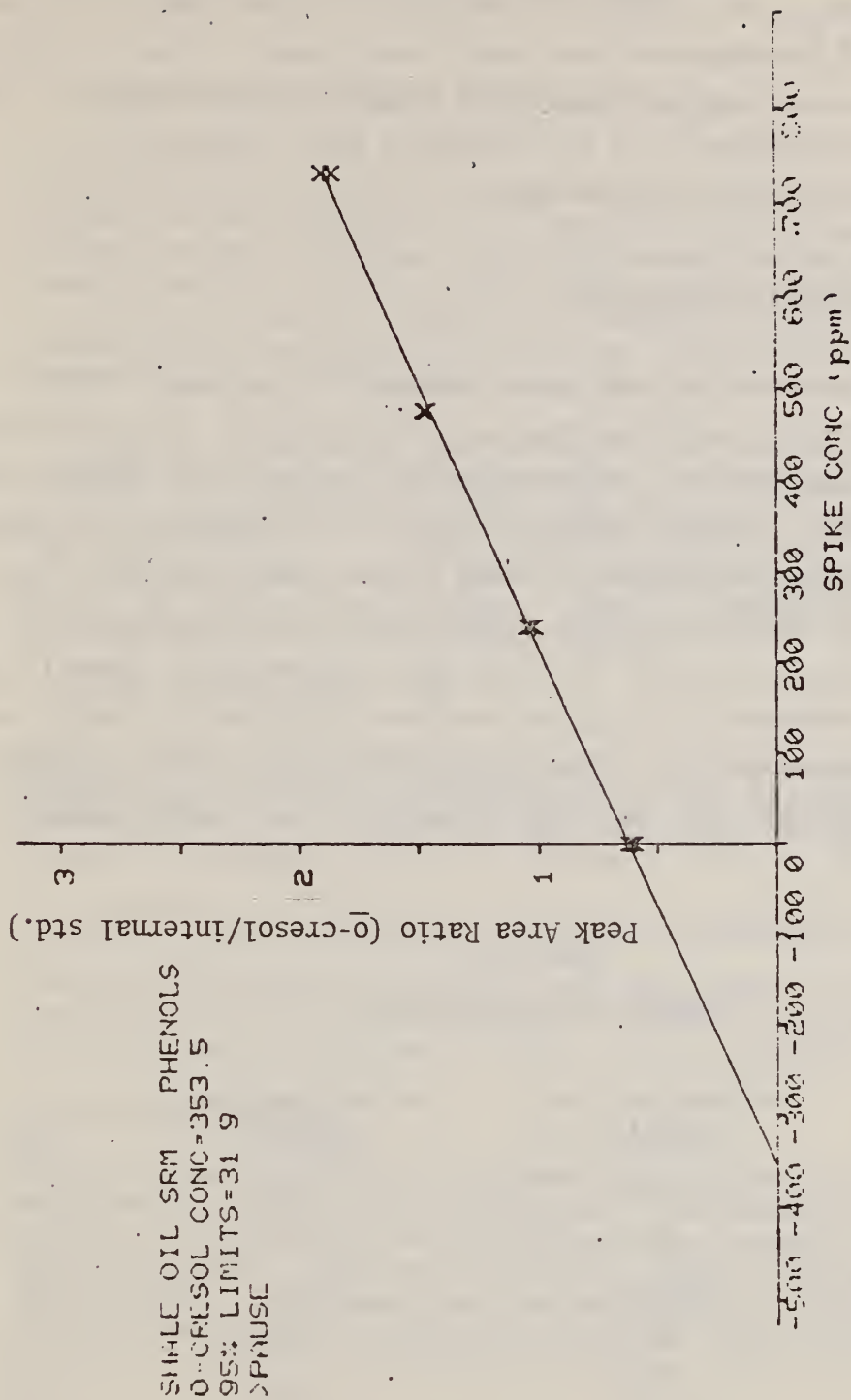
Figure 13. Standard addition quantitation of o-cresol in shale oil.

SHALE OIL SRM   PHENOLS
O-CRESOL CONC=353.5
95% LIMITS=31 9
>PAUSE

In some of our earlier studies (reported previously) on the stability of aqueous solutions of phenols, losses possibly due to adsorption and biodegradation have been found. Due to these results, it is essential to conduct a study of stability of some carefully selected phenols in a distilled water matrix to ascertain the possibility of an SRM.

1.d. Interlaboratory Comparison

During the past six months NBS participated in a round robin exercise to determine interlaboratory precision in the measurement of phenols in wastewaters. Eight samples containing phenol were received from ASTM. These samples were to be analyzed for phenols using the procedure described in ASTM D1783, and the pH of the samples was to be measured also. Preliminary determinations were made on the samples in order to find the approximate phenol concentration. A thousand-fold dilution was required in order to bring the concentration into the range for which the procedure is valid. Concentrations and pHs found for the eight samples follow in Table 8.

Table 8

Phenol Concentrations

Sample No.	Determination A (mg/L)	Determination B (mg/L)	pH
1	40	40.4	8.5
2	20	20	4.1
3	3520	3710	8.8
4	65.2	66.4	8.4
5	35.8	35.6	4.1
6	4520	4520	8.8
7	2900	2950	3.7
8	124	127	4.0

80-BCN-ENERGY RELATED POLLUTANTS AND EFFECT MONITORING AND ASSOCIATED
METHODS AND TECHNIQUES DEVELOPMENT

1. Radiological Pollutant Quality Assurance

The assessment of regional and national effects of radionuclides
depends on the comparability of empirical data generated throughout
the new energy developing industries as well as the existing nuclear
power industry. The major goal of this program element is to develop
an optimum radiological monitoring program to provide validated radio-
logical environmental quality baseline data in those geographical areas
where new energy developments impact on the environment.

The primary objective of the NBS program is to provide measurement
traceability, for certain radionuclides not included in other programs,
to the U. S. Environmental Protection·Agency at Las Vegas (EPA-LV)
and, through EPA-LV, to other laboratories. Specific radionuclides
are chosen for the program because they are released into the environ-
ment from nuclear power reactors (such as light-water reactors), coal
burning plants, or other related sources.

1.a   Solution of Plutonium - 241

We are continuing to measure the half life of plutonium-241 by
means of α-γ-coincidence measurements of the in-growth of
americium-241. Our results to date are consistent with the
generally accepted value of 14.35 years.

1.b   Fly Ash from Coal Combustion Assayed for Radium-226 and Radium-228

Two hundred samples of 100 grams each were sent to EPA-LV. The
Report of Calibration has been completed and submitted to EPA-LV
for distribution with the fly ash. A copy is attached as Appendix 1.

1.c   Thorium-232 Solution

At the request of EPA-LV in October, NBS assayed the thorium-232
solution for radionuclidic impurities. Radium-226 was assayed by
gamma-ray spectrometry cf its shorter-lived progeny in equilibrium
with radium-226. Thorium-230 is being assayed by alpha-particle
spectrometry. The assays and the preparation of the Report of
Calibration should be completed during the first half of 1980.

1.d   Mixed Radionuclide Solutions

Two mixed radionuclide solutions have been prepared, each containing
tritium, strontium-90, cesium-134, radium-226, radium-228, and
uranium of natural isotopic composition. One solution is a ten-
fold dilution of the other. Two hundred 5-ml ampoules of each
solution have been produced for distribution by EPA-LV. Checks on
the production of these standards are underway, and the Reports of
Calibration are being written.

2.   Measurement Traceability Studies with Analytical Quality Control
      of EPA-LV

The NBS conducts tests with Analytical Quality Control (AQC),
formerly the Quality Assurance Branch, to ascertain whether radio-
activity measurements made by AQC are traceable to NBS. These
studies use radioactive reference test samples, with known but
undisclosed values, that are sent to AQC by NBS, and radioactivity
standards prepared by AQC and sent to NBS for confirmatory measurements.
Technical personnel of EPA and NBS decided, at a December meeting in
Washington, that in the future there will be more emphasis on the
checking by NBS of radioactivity standards calibrated and distributed
by EPA-LV. The criteria for conducting the studies are given in an
appendix to the NBS-EPA interagency agreement of April 1976.

During the period of July 1979 through December 1979, NBS
provided AQC with seven solution reference samples and received
four results from AQC, which are listed in Table 9. Copies
of the Reports of Traceability Measurements are attached as
Appendices 2 through 5.

TABLE 9

Reference Samples with Known, but Undisclosed, Values Provided to EPA-LV by NBS, July through December, 1979

Parent Radionuclides	Month Sent
Mixed radionuclides	July
Phosphorous-32	November
Scandium-46	December
Tin-113	July
Iodine-131	July
Promethium-147	October
Bismuth-207	August

Results Reported by EPA-LV to NBS, July through December, 1979

Parent Radionuclide	AQC/NBS
Cobalt-58	0.961
Cerium-141	1.080
Lead-203	1.17
Plutonium-238	1.000

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

WASHINGTON, D.C.   20234

Appendix 1

REPORT OF CALIBRATION

FLY ASH FROM COAL COMBUSTION

FOR ASSAYS OF RADIUM-226 AND RADIUM-228

This sample consists of approximately 100 grams of fly ash, from the combustion of eastern United States coal, in a screw-cap glass jar. The sample is from a batch of fly ash that had been passed through a 170-mesh sieve (90-μm openings) and then mixed for two hours. The tests for homogeneity are described in the Supplemental Information section of this Report.

The radioactivity concentration of radium-226 per unit mass of fly ash in May 1979 was

$$*0.130 \ s^{-1}g^{-1} \pm 6.6\%*.$$

Five weighed samples of the fly ash from one 100-g sample were assayed for radium-226 by radiochemically separating radium, removing the radon-222 from the radium solution, and measuring the alpha-particle-emission rate of the radon and its short-lived progeny in the NBS radon pulse-ionization chambers. In order to confirm this result, the emission rates of gamma-rays from the decay of lead-214 and bismuth-214 were measured with a calibrated Ge(Li)-detector spectrometer. The radioactivity concentration of radium-226 thus derived agreed with the certified value to within three percent. Details of the assay methods are given in the Supplemental Information section.

The uncertainty in the radium-226 radioactivity concentration, 6.6%, is the linear sum of 1.1 percent, which is the limit of the random error of the pulse-ionization-chamber measurements at the 99-percent confidence level ($4.604 \ S_m$, where S_m is the standard error computed from a total of 22 measurements of five samples), and 5.5 percent, which is the linear sum of the estimated limits of conceivable systematic errors, including 3 percent for inhomogeneity, and 1.0 percent in the efficiency calibration of the pulse-ionization chambers. The stated uncertainty is for a sample size of 10 grams or greater.

The radioactivity concentration of radium-228 per unit mass of fly ash in May 1979 was

$$*9.5 \times 10^{-2} \ s^{-1}g^{-1} \pm 14\%*.$$

Twelve weighed samples of the fly ash were assayed for radium-228 by measuring the emission rates of gamma rays from the decay of radium-228 progeny, which were in radioactive equilibrium with radium-228, using a Ge(Li)-detector spectrometer. The detector was calibrated using a weighed fly-ash sample that had been quantitatively spiked with a calibrated gamma-ray-emitting solution. Details of the assay method are given in the Supplemental Information section.

The uncertainty in the radium-228 radioactivity concentration, 14 percent, is the linear sum of 1.6 percent, which is the statistical uncertainty in the Ge(Li)-detector measurements (three times the standard error of the weighted mean), and $12._1$ percent, which is the linear sum of the estimated limits of conceivable systematic errors. Estimated limits of systematic errors include 3 percent for inhomogeneity, 4.5 percent for uncertainties in the values of the gamma-ray-probabilities per decay, and 4.5 percent in the efficiency calibration curve for the Ge(Li) detector. The stated uncertainty is for a sample size of 10 grams or greater.

The radioactivity concentration of radium-228 derived from measurements of emission rates of gamma rays from the decay of actinium-228 differs by only three percent from the radioactivity concentration of radium-228 derived from measurements of emission rates of gamma rays from the decay of bismuth-212 and thallium-208. Thus thorium-228 is, within the limits of the experimental uncertainty, in radioactive equilibrium with radium-228 in the fly ash.

In September, 1978, 13 samples of fly ash were assayed for radium-228 using a Ge(Li)-detector spectrometer, and a value for the radioactivity concentration was obtained that differed by only three percent from the certified value. Thus radium-228 is, within the limits of the experimental uncertainty, in radioactive equilibrium with thorium-232, and, analogously, radium-226 is probably in equilibrium with thorium-230. Because these two thorium isotopes have very long half lives, no decay corrections to the certified radium values will be necessary.

Prior to the weighing of working quantities of this material, they should be dried in air at 40 °C for at least 24 hours.

When measuring emission rates of gamma rays from the decay of lead-214 and bismuth-214, the sample should be in a closed, air-tight container for at least a month prior to the assay, to ensure radioactive equilibrium with radium-226. When measuring emission rates of gamma rays from the decay of lead-212, bismuth-212, and thallium-208, the sample should be in a closed, air-tight container for at least four days prior to the assay, to ensure radioactive equilibrium with radium-224.

For the Director,

W. B. Mann, Chief
Radioactivity Section
Center for Radiation Research

July 1979

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SUPPLEMENTAL INFORMATION

Testing for Homogeneity

The fly ash was provided through the courtesy of the NBS Office of Standard
Reference Materials. From the 220 100-gram samples that were prepared, ten
percent were randomly selected and checked for homogeneity of gamma-ray-
emitting nuclides. These 22 samples were weighed into specially designed,
glass jars with plate glass bottoms and ground glass stoppers. The jars
were tapped until the samples occupied approximately equal volumes with a bulk
density of 1.1 g cm^{-3}, and the stoppers were sealed with wax. Each sample was
counted for 10,000 seconds, live time, in a well-type NaI(Tl)-detector spec-
trometer. The gamma-ray-emission rates from each sample were compared, using
pulse-height analysis, over five discrete energy regions containing the larger
photopeaks, and also over one region which comprised most of the gamma-ray
spectrum. No sample gave outlying results, based on a criterion discussed
by Natrella (1), using 0.05 as the value for alpha.

In order to check the homogeneity within a 100-gram sample, one was divided
into ten accurately weighed samples of about 10 grams each in plastic vials.
Each of these 10-gram samples was counted for 20,000 seconds, live time, in
a well-type NaI(Tl)-detector spectrometer. The gamma-ray-emission rates were
compared as before except that six, rather than five, discrete energy regions
were used. Again, there were no outlying results, based on the same criterion.

The sample-to-sample inhomogeneity, for each energy region, was defined as the
range of the measured gamma-ray-emission rates for all the examined samples of
a particular size, minus the range of the measured gamma-ray-emission rates
from an equal number of repetitive measurements on a single sample of that
size. The sample-to-sample inhomogeneity in any of the energy regions, expressed
as a percent of the mean of the gamma-ray-emission rates for all the samples
tested of a given size, was no more than 3.1 percent for either the 100-gram
samples or the 10-gram samples.

Assay for Radium-226

The fly-ash sample that had been divided into 10-gram samples for homogeneity
testing was chosen to be radiochemically assayed for radium-226. Accurately
weighed samples of about five grams each were processed by a procedure de-
scribed in EML-300 (2). After processing each sample, its chemical yield was
measured by counting the barium-133 tracer in the solution, using a well-type
NaI(Tl)-detector spectrometer. The amount of tracer initially added to each
sample was chosen to provide a gamma-ray count rate after processing of between
60 and 90 per second under the 356-keV photopeak of cesium-133.

Following the determination of the chemical yield, the sample was transferred
to a radon bubbler, and a few drops of 1-octanol were added to prevent foaming
during de-emanation. The sample was de-emanated, and radon was allowed to
collect for a period of 10 to 18 days. The solution was then again de-emanated,

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and this radon was transferred by nitrogen, which had been bottled for at least
a month, through a gas-handling system into an NBS pulse-ionization chamber,
as described by Harding et alia (3). Four chambers were used, each of which
was calibrated three times with an NBS radium-226 solution standard (Standard
Reference Material 4953). Each sample was counted one or more times in at
least three different chambers.

Each determination consisted of a series of consecutive 1000-second counts
over a period of one to several days. This series was started after polonium-214
was observed to have reached radioactive equilibrium with radon-222 in the pulse-
ionization chamber. The same procedure was followed when measuring the chamber
backgrounds, using pure nitrogen. Each net sample count was corrected for the
decay of radon-222 that occurred during the time of collection and counting, using
a half life of 3.824 days. The radium-226 activity per gram of fly ash was then
calculated, with corrections for the chemical yield and the radium content of the
chemical reagents. The total radium-226 content in the quantities of the reagents
used to process a 5-gram sample of fly ash (the reagent blank) was assayed in the
same manner as the fly-ash samples. The mean value from six assays was used as the
correction.

A confirmatory measurement for radium-226 was made in the manner described
below for radium-228. The following gamma-ray photopeaks were used for these
radium-226 assays: 295 and 352 keV from the decay of lead-214; and 609, 768,
1120, 1238, and 1765 keV from the decay of bismuth-214.

Assay for Radium-228

Twelve of the 100-gram samples of fly ash that had been tested for homogeneity
were assayed by gamma-ray spectrometry for radium-228. The jars had been sealed
for at least a month so that radium-226 could be assayed at the same time, using
its gamma-ray-emitting progeny. The gamma-ray-emission rates were measured with
each jar sitting on a 65-cm^3 Ge(Li)-detector spectrometer inside a mercury-filled
shield for 64,000 seconds, elapsed time, and the gamma-ray spectra were stored
on magnetic tape. A pulse generator was used to determine the dead-time correction.
Background spectra, of a jar filled with an equal volume of distilled water, were
similarly accumulated.

Prior to the final data analysis, the spectra from each set were summed. The
locations and areas of the gamma-ray photopeaks, for samples and for backgrounds,
were determined by a computer program (4). Radionuclides were identified and net
count rates calculated.

The radioactivity concentrations of several progeny of radium-228 were computed
using gamma-ray-emission probabilities per decay that were compiled by Kocher (5),
and a Ge(Li)-detector-efficiency curve derived from a weighed 100-gram sample of
fly ash that had been quantitatively spiked with an NBS-calibrated solution con-
taining nine gamma-ray-emitting nuclides. The spiking procedure, which was based
on work by Sill and Hindman (6), was carried out in a glove bag. The spiked
material was found to be homogeneous by measurements with a NaI(Tl)-detector
spectrometer of the gamma-ray-emission rates from accurately weighed samples of
about 10 grams each. When used to determine the Ge(Li)-detector efficiency, the

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spiked samples were measured in the same counting geometry as were the unspiked samples.

The reported radioactivity concentration of radium-228 is the weighted mean of radioactivity concentrations derived from these photopeaks: 463, 795, 911, and 969 keV from the decay of actinium-228; 727 keV from the decay of bismuth-212; and 583 and 860 keV from the decay of thallium-208. The weights were the reciprocals of the variances of the net count rates. A value of 0.3593 was used for the alpha-particle branching ratio in the decay of bismuth-212 (5).

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U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

Appendix 2

National Bureau of Standards

Report of Traceability Measurement by

QUALITY ASSURANCE BRANCH
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA

on an NBS Reference Sample of Undisclosed Value of

COBALT-58

This is to report that on the basis of nine measurements with a Ge(Li)-detector spectrometer of the emission rate of the 811-keV gamma ray from the decay of cobalt-58 in a solution reference sample of known, but undisclosed, total radio-activity, at 0700 EST September 1, 1978, of

$$*1.343 \times 10^6 \ s^{-1} \pm 2.9\%*,$$

the Quality Assurance Branch (QAB) reported a value of
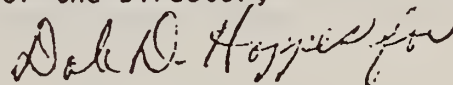
$$1.29 \times 10^6 \ s^{-1} \pm 5.5\%$$

at 0700 EST September 1, 1978.

The QAB value differs from the NBS value by 3.9 percent. This result demonstrates traceability of QAB to NBS for this measurement to within five percent, as specified in the appendix, "Traceability Studies", of the EPA-NBS interagency agreement of April 20, 1976.

Supplemental information about this reference sample is on the attached sheet.

For the Director,

W.B. Mann, Principal Scientist
Radioactivity laboratory
Center for Radiation Research

September 17, 1979

The reference sample consisted of cobalt-58 in 5.21380 grams of carrier solution in a flame-sealed borosilicate-glass ampoule. The solution contained 50 micrograms of stable cobalt per gram of 4 molar hydrochloric acid, and was a quantitative dilution of a master solution, the radioactivity concentration of which was measured relative to a radium-226 reference source in the NBS "4π"γ pressure ionization chamber. The ionization chamber had previously been calibrated using cobalt-58 solutions that were calibrated by NaI(Tl) counting.

The material from which the master solution was prepared was examined for photon-emitting impurities with a Ge(Li)-detector spectrometer, and only cobalt-57 and cobalt-60 were found. As of September 1, 1978 the ratios of the activity of each impurity nuclide to that of cobalt-58, found by NBS and QAB, were:

IMPURITY	NBS	QAB
cobalt-57	$8.9 \times 10^{-3} \pm 20\%$	8.1×10^{-3}
cobalt-60	$5.2 \times 10^{-3} \pm 20\%$	4.9×10^{-3}.

The detection limits for impurity photons can be expressed as a percentage of the emission rate of the 811-keV gamma ray emitted in the decay of cobalt-58. These limits for NBS are 0.1 percent for gamma rays with energies greater than 90 keV and less than 806 keV, and 0.01 percent for those with energies between 816 and 1900 keV, provided that the impurity photons are separated in energy by 5 keV or more from photons of equal or greater intensity emitted in the decay of cobalt-58.

A half life of 70.80 ± 0.08 days [NCRP Report No. 58, Appendix A, National Council on Radiation Protection and Measurements, Washington, 1978] was used to calculate the NBS value for the cobalt-58 radioactivity of the reference sample at the time of measurement by QAB. The total uncertainty in the NBS value, 2.9 percent, is the linear sum of the uncertainty in the radioactivity concentration value of the master solution (2.7 percent), the uncertainty in the decay correction (0.1 percent), and the systematic error associated with the dilution (0.1 percent).

Appendix 3

National Bureau of Standards

Report of Traceability Measurement by

QUALITY ASSURANCE BRANCH
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA

on an NBS Reference Sample of Undisclosed Value of

CERIUM-141

This is to report that on the basis of 18 measurements with a Ge(Li)-detector spectrometer on nine sources prepared from a solution of cerium-141 with a known, but undisclosed, radioactivity concentration at 0700 EST August 25, 1978, of

$$*6.611 \times 10^5 \ s^{-1}g^{-1} \pm 2.5\%*,$$

the Quality Assurance Branch (QAB) reported a value of

$$7.14 \times 10^5 \ s^{-1}g^{-1} \pm 3.4\%$$

at 0700 EST August 25, 1978.

The QAB value differs from the NBS value by 8.0 percent. The result demonstrates traceability of QAB to NBS for this measurement to within eight percent, but does not lie within five percent of the NBS value as specified in the appendix, "Traceability Studies", of the EPA-NBS interagency agreement of April 20, 1976.

Supplemental Information about this cerium-141 reference sample is provided on the attached sheet.

For the Director,

W. B. Mann

W. B. Mann, Chief
Radioactivity Section
Center for Radiation Research

August 6, 1979

SUPPLEMENTAL INFORMATION

for

CERIUM-141 REFERENCE SAMPLE

This reference sample consisted of cerium-141 in 5.327 grams of carrier solution in a flame-sealed borosilicate-glass ampoule. The carrier solution contained 66 micrograms of stable cerium per gram of 4 molar hydrochloric acid.

The radioactivity concentration of the master solution from which the reference sample was prepared was measured, relative to a radium-226 reference source, in the NBS "4π"γ pressure ionization chamber. The ionization chamber had previously been calibrated, in terms of a radium-226 reference source, with cerium-141 solutions which had been calibrated by $4\pi\beta$-γ coincidence counting.

The material from which the master solution was prepared was examined for photon-emitting impurities with germanium spectrometer systems, and only cerium-139 was found. On August 25, 1978, the ratio of the radioactivity concentration of cerium-139 to that of cerium-141 was 0.0065 ± 5%.

The detection limits for impurity photons can be expressed as a percentage of the emission rate of the 145-keV gamma ray emitted in the decay of cerium-141. These limits are 0.1 percent for gamma rays with energies greater than 20 keV and less than 140 keV, and 0.01 percent for those with energies between 150 and 1900 keV, provided that the impurity photons are separated in energy by 5 keV or more from photons of equal or greater intensity emitted in the decay of cerium-141.

A half-life value of 32.501 ± 0.005 days was used for the decay correction (NCRP Report No. 58, Appendix A, National Council on Radiation Protection and Measurements, Washington, 1978).

National Bureau of Standards

Report of Traceability Measurement by

QUALITY ASSURANCE BRANCH
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA

on an NBS Reference Sample of Undisclosed Value of

LEAD-203

This is to report that on the basis of 20 measurements with a Ge(Li)-detector spectrometer of the emission rate of the 279-keV gamma ray from the decay of lead-203 in a solution reference sample with a known, but undisclosed, total radioactivity at 0700 EST November 22, 1978, of

$$*2.348 \times 10^6 \text{ s}^{-1} \pm 2.20\%*,$$

the Quality Assurance Branch (QAB) reported a value of

$$2.75 \times 10^6 \text{ s}^{-1} \pm 5.3\%$$

at 0700 EST November 22, 1978.

The QAB value differs from the NBS value by 17 percent, and does not lie within five percent of the NBS value as specified in the appendix, "Traceability Studies", of the EPA-NBS interagency agreement of April 20, 1976.

The reference sample was ampoule number 16 of NBS Standard Reference Material 4420L, the certificate for which is attached. A half life of 52.05 ± 0.10 hours was used in the decay correction from the time of calibration to the time of measurement by QAB (NCRP Report No. 58, "A Handbook of Radioactivity Measurements Procedures", appendix A, National Council on Radiation Protection and Measurements, Washington, 1978).

The uncertainty in the NBS value of the total activity of the reference sample, 2.20 percent, is the linear sum of the uncertainty in the radioactivity concentration of SRM 4420L (1.67 percent), the uncertainty in the mass of solution in the ampoule (0.05 percent), and the uncertainty in the decay correction (0.48 percent).

For the Director,

signature

W.B. Mann, Principal Scientist
Radioactivity laboratory
Center for Radiation Research

September 17, 1979

National Bureau of Standards
Certificate
Standard Reference Material 4420L
Radioactivity Standard
Lead-203

This Standard Reference Material consists of lead-203 in *5.0130* grams of carrier solution in a flame-sealed borosilicate-glass ampoule. The solution contains approximately 8 micrograms of lead per gram of approximately 0.5 molar hydrochloric acid and has a density of 1.007 ± 0.002 grams per milliliter at 20.2°C.

The radioactivity concentration of the lead-203 as of 1830 EST November 16, 1978, was

$$*2.735 \times 10^6 \text{ s}^{-1}\text{g}^{-1} \pm 1.67\%*.$$

This Standard Reference Material was measured, relative to a radium-226 reference source, in the National Bureau of Standards "4π"γ pressure ionization chamber which had previously been calibrated, in terms of a radium-226 reference source, with lead-203 solutions from which quantitative sources had been prepared and $4\pi(e,x)-\gamma$ coincidence counted using the efficiency extrapolation method.

The solution from which this Standard Reference Material was prepared was examined for photon-emitting impurities with germanium-spectrometer systems and thallium-200, thallium-201 and lead-201 were found to be present. As of the certification time, the ratios of the activity of each impurity nuclide to that of the principal radionuclide were

thallium-200	$3.3 \times 10^{-5} \pm 60\%$
thallium-201	$2 \times 10^{-3} \pm 60\%$
lead-201	$5.0 \times 10^{-4} \pm 20\%$.

The detection limits for impurity photons may be expressed as a percentage of the gamma-ray-emission rate of the 279-keV gamma ray emitted in the decay of lead-203. These limits are 0.1 percent for gamma rays with energies greater than 90 keV and less than 279 keV, and 0.01 percent for those between 284 and 1900 keV, provided that the impurity photons are separated in energy by 5 keV or more from photons of equal or greater intensity emitted in the decay of lead-203.

The uncertainty in the radioactivity concentration, 1.67 percent, is the linear sum of 0.02 percent, which is the limit of the random error at the 99-percent confidence level (2.898 S_m, where S_m is the standard error of the mean computed from independent measurements of 18 samples) and 1.65 percent, which is the estimated upper limit of conceivable systematic errors.

This Standard Reference Material was prepared in the Center for Radiation Research, Nuclear Radiation Division, Radioactivity Section, W. B. Mann, Chief.

SRM 4420L-

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler. Director

National Bureau of Standards

Report of Traceability Measurement by

QUALITY ASSURANCE BRANCH
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA

on an NBS Reference Sample of Undisclosed Value of

PLUTONIUM-238

This is to report that on the basis of 20 measurements with 1π and 4π proportional counters on a point source of plutonium-238 with a known, but undisclosed, radioactivity on March 9, 1979, of

$$*385.0 \ s^{-1} \pm 1.5\%*,$$

the Quality Assurance Branch (QAB) reported a value of

$$385 \ s^{-1} \pm 2.8\%$$

on March 9, 1979. The random component of the reported QAB uncertainty, 1.1 percent, is the standard error of the mean at the 99-percent confidence level. The estimated upper limits of conceivable systematic errors were linearly added to the random component.

The QAB value does not differ from the NBS value. This result demonstrates traceability of QAB to NBS for this measurement to within five percent as specified in the appendix "Traceability Studies" of the NBS-EPA interagency agreement of April, 1976.

This reference sample is Standard Reference Material 4906-B-4, the certificate for which is attached.

For the Director,

W. B. Mann, Principal Scientist
Radioactivity Group
Center for Radiation Research

January 7, 1980

Attachment

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National Bureau of Standards
Certificate
Standard Reference Material 4906-B
Alpha-Particle Standard
Plutonium-238

This Standard Reference Material consists of a practically weightless source of plutonium-238 electroplated onto a 0.010-cm-thick platinum foil 0.6 cm in diameter, which is cemented to a monel disk 2.54 cm in diameter and 0.16-cm thick.

The activity of the plutonium-238 at 1200 EST, July 1, 1978, was

$$* \quad 3.871 \times 10^{2} \quad s^{-1} \pm 1.5\% *.$$

This Standard Reference Material was calibrated in the National Bureau of Standards "0.8π"α counter, which has an accurately known geometry.

The uncertainty in the activity, 1.5 percent, is the linear sum of 0.9 percent, which is the limit of the random error at the 99-percent confidence level (3.499 S_m, where S_m is the standard error computed from eight measurements), and 0.6 percent, which is the sum of the estimated upper limits of conceivable systematic errors.

The solution from which this Standard Reference Material was prepared was examined for gamma-ray-emitting impurities with a germanium-spectrometer system and gamma rays with an energy of 59.6 keV were observed. If one assumes that the 59.6-keV gamma rays are produced in the electron-capture decay of plutonium-237 impurity atoms, the ratio of the activity of plutonium-237 to that of plutonium-238 on August 8, 1977, was 7×10^{-4}. No other gamma-ray-emitting impurities were found. It is estimated that any photons between 20 and 400 keV would have been detected if their emission rate were greater than 0.1 percent that of the 44-keV photons from the decay of plutonium-238 and were different in energy by at least 5 keV from any photons emitted in the decay of plutonium-238.

A source made from the material was examined for alpha-particle-emitting impurities with a silicon surface-barrier detector and none were observed. It is estimated that alpha particles from impurity radionuclides would be detected if the emission rate were greater than 10^{-4} of the plutonium-238 alpha-particle-emission rate. The alpha-particle-energy resolution of the silicon surface-barrier detector used in the impurity measurement is 25 keV.

A half life of 87.74 ± 0.04 years is suggested.[+]

This Standard Reference Material was prepared and calibrated in the Center for Radiation Research, Nuclear Radiation Division, Radioactivity Section, W. B. Mann, Chief.

Washington, D.C. 20234
July, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

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SRM 4906-B- 4

[+]Diamond H., Bentley W.C., Jaffey A.H. and Flynn K.F., Phys. Rev. C 15, 1034 (1977).

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Washington, DC 20460

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15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

This semi-annual report describes the progress during the period July – December 1979 on the work performed by the National Bureau of Standards under an interagency agreement between the U. S. Environmental Protection Agency and the National Bureau of Standards. The report consists of specific subagreements dealing with the development of standards for the measurement of pollutants associated with energy production and use.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Air; Coal; Energy; Gases; Instrumentation; Monitoring; Particulates; Petroleum; Pollution; Quality Assurance; Radiological Pollutant; SRM's; Sulfur; Water

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